4-30-2018

New Polyether Complexes of Germanium(II) and Tin(II): Synthesis, Structural Characterization and Reactivity

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New Polyether Complexes of Germanium(II) and Tin(II):

Synthesis, Structural Characterization and Reactivity

By

Alina Maria Secara

A Thesis
Submitted to the Faculty of Graduate Studies
through the Department of Chemistry and Biochemistry
in Partial Fulfillment of the Requirements for
the Degree of Master of Science at the University of Windsor

Windsor, Ontario, Canada

2018

New Polyether Complexes of Germanium(II) and Tin(II): Synthesis, Structural Characterization and Reactivity

by

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April 26, 2018

Declaration of Co-Authorship/Previous Publication

I. Co-Authorship

I hereby declare that this thesis incorporates material that is result of joint research, as follows:

Chapter 2 and **3** contain results included in the manuscript accepted for publication entitled "Synthesis and Structural Characterization of New Polyether Complexes of Germanium(II) and Tin(II)" (Alina M. Secara, Justin F. Binder, Ala'aeddeen Swidan and Charles L.B. Macdonald, Canadian Journal of Chemistry, **2018**). I and Justin F. Binder prepared the manuscript. Justin F. Binder performed the X-ray crystallography experiments. I synthesized and further characterized all the complexes in this work. Ala'aeddeen Swidan performed the X-ray crystallography experiment for the water adduct ($H_2O{\cdot}SnOTf(dibenzo[24]crown\text{-}8)][OTf]$) presented in chapter **3** and the elemental analysis. My supervisor, Dr. Charles L.B. Macdonald refined and solved the crystal structures and provided significant edits to the manuscript.

Chapter 4 contains the preliminary results of the investigation into reactivity of the new polyether complexes. I synthesized and characterized all the compounds in this work. Ala'aeddeen Swidan performed the elemental analysis for one of the compounds ($C_{26}H_{32}F_6Sn_2O_{14}S_2$) in this work. The results presented in this chapter are unpublished.

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This thesis includes 1 original papers that have been previously published/submitted for publication in peer reviewed journals, as follows:

Thesis Chapter	Publication title/full citation	Publication status
Chapter 2	"Synthesis and Structural Characterization of New Polyether Complexes of Germanium(II) and Tin(II)", **Alina M. Secara**, Justin F. Binder, Ala'aeddeen Swidan and Charles L.B. Macdonald, *Canadian Journal of Chemistry,* **2018**	Accepted
Chapter 3	"Synthesis and Structural Characterization of New Polyether Complexes of Germanium(II) and Tin(II)", **Alina M. Secara**, Justin F. Binder, Ala'aeddeen Swidan and Charles L.B. Macdonald, *Canadian Journal of Chemistry,* **2018**	Accepted

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Abstract

The chemistry involving group 14 cations and polyether ligands has been an area of great interest in the last decade. The Macdonald Group has long been interested in the synthesis, characterization and reactivity of polyether complexes containing group 13 and 14 elements in low oxidation state. Recently, our group has demonstrated that the properties of crown ethers and of the more flexible glyme ligands make them ideal for the stabilization of group 14 elements in the +2 oxidation state. Many of the resulting polyether complexes hold great potential for further reactivity in that they may act as Lewis acids to simple nucleophiles like water and ammonia while retaining a non-bonding electron pair.

A series of complexes of crown ethers and glymes with Ge(II) and Sn(II) bromide have been synthesized. Specifically, [GeBr([15]crown-5)][$GeBr_3$], [GeBr([18]crown-6)][$GeBr_3$], [GeBr(triglyme)][$GeBr_3$], [GeBr(tetraglyme)][$GeBr_3$], [SnBr([18]crown-6)][$SnBr_3$], [Sn([15]crown-5)$_2$][$SnBr_3$]$_2$, [SnBr(triglyme)][$SnBr_3$] and [SnBr(tetraglyme)][$SnBr_3$] have been fully characterized including by single crystal X-ray diffraction. [GeBr(triglyme)][$GeBr_3$] and [GeBr(tetraglyme)][$GeBr_3$] represent the first examples of crystallographically confirmed glyme complexes of germanium. The synthesis of [GeBr(dibenzo[24]crown-8)][$GeBr_3$] and [GeCl(dibenzo[24]crown-8)][$GeCl_3$] are also reported, along with the crystal structure of the latter's water adduct, which features the water molecule adjacent to the $GeCl^+$ ion within the cavity of the crown ether. Recrystallization of the salt [SnOTf(dibenzo[24]crown-8)][OTf] generated crystals of the water complex suitable for examination by single crystal X-ray diffraction.

Dedication

Dedicated to my loving husband Tudor and

my wonderful daughters, Teodora and Alexandra!

Acknowledgements

Since my graduation from university, my life has changed and become drastically different. Immigrating to Canada was one of the most significant events of my life; however, while my life in a new country progressed very quickly, one of my biggest dreams of continuing my education seemed to progressively fade as the years passed by. Because of this, I would like to express my sincere gratitude to Dr. Chuck Macdonald, my supervisor. I am very grateful to him for this special opportunity, as it has allowed me to reconnect and continue pursuing my aspirations, as well as obtaining my masters. I would like to thank Chuck especially for his patience, encouragement and guidance, and for all the advice he has given me – including the mini chemistry lessons when a question arose. Thank you very much for everything!

I would like to thank Dr. Steve Loeb and Dr. Joel Gagnon for agreeing to be on my examination committee and for taking the time to read my thesis.

I would like to thank all the Macdonald group members, past and present. Special and sincere thanks go to Justin for his continued support regarding my research work and especially for my first crystal structure, AMS 22. Also, special thanks go to Ala for always being a great help. I would like to thank Steph for helping me get started in the lab and for all the help during these two years. Thank you to Fawzia for being a good colleague and for all the talks we had, also to Emily, Max, Brad and Lara. I would also like to thank Zeinab and Mitch from the Rawson group for their helpful advice.

Extended thanks go to Dr. Matt Revington for his help and guidance with NMR spectroscopy and Dr. Janeen Auld for EA. Thank you to Marlene for always keeping us on track and to Beth for all the nice conversations we had. Thank you to Nedhal for her encouragement.

I would also like to thank the great professors that I have had, especially Dr. Steve Loeb, Dr. Jeremy Rawson and Dr. Tricia Charmichael for their awesome work. Especially, to Dr. Loeb for his patience and for listening to my first presentation, probably one of the longest presentations in his class.

Most importantly, I wish to thank my loving and supportive husband, Tudor and my two wonderful daughters, Teodora and Alexandra for their unending love, understanding and encouragement. Especially to you Tudor, I would not have accomplished any of this without you!

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List of Schemes

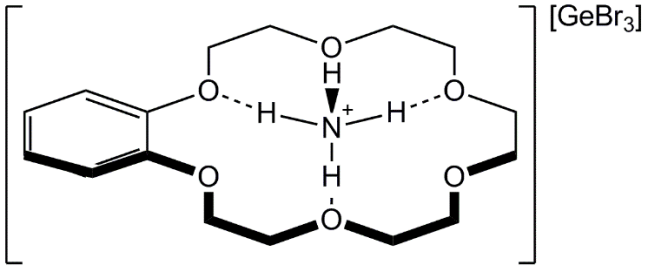
List of Abbreviations/Symbols

[12]crown-4	1,4,7,10-tetraoxacyclododecane
[15]crown-5	1,4,7,10,13-pentaoxacyclopentadecane
[18]crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
Å	Angstrom
Anal. Calc.	Analytically Calculated
Benzo[18]crown-6	2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine
^{13}C	carbon-13
cm	centimeter
CSD	Cambridge Structural Database
δ	Chemical Shift (NMR)
CD_3CN	acetonitrile-d_3
DCM	Dichloromethane
deg (or °)	degrees
Dibenzo-24-crown-8	6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosine
E	Element
Et_2O	diethyl ether
^{19}F	fluorine-19
FT-IR	Fourier transform infrared spectroscopy
^{1}H	proton
g	gram
Hz	Hertz
^{i}Pr	Iso-propyl
IUPAC	International Union of Pure and Applied Chemistry
m	Multiplet (NMR)
Me	Methyl, CH_3

MeIm	*N*-methylimidazole
mg	milligram
mL	milliliter
mm	millimeter
mmol	millimole
Mp	Melting point
^{14}N	14N nitrogen-14
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
OTf	Triflate, $SO_3CF_3^-$, trifluoromethanesulfonate
p	Pentet (NMR)
ppm	parts per million
R	organic substituent
Redox	reduction-oxidation
s	Singlet (NMR)
SC-XRD	Single Crystal X-ray Diffraction
t	Triplet (NMR)
THF	Tetrahydrofuran
Triflate	Trifluoromethanesulfonate
X	Halogen atom

List of Complexes

Chapter 2



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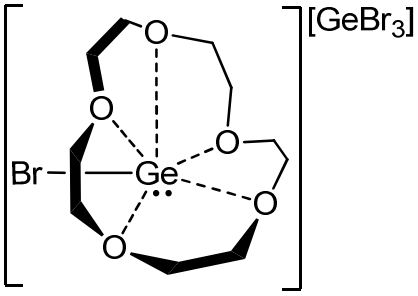

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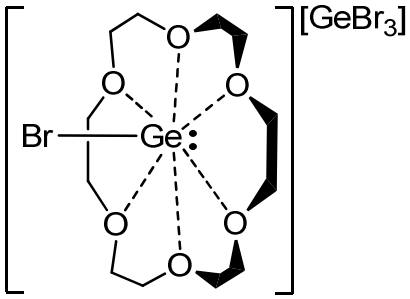

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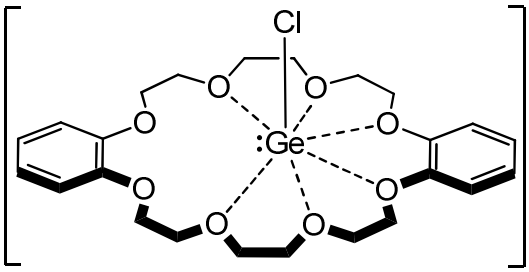

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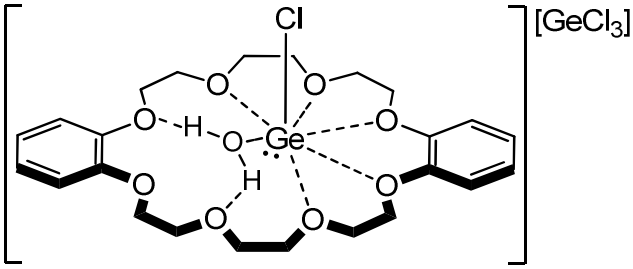

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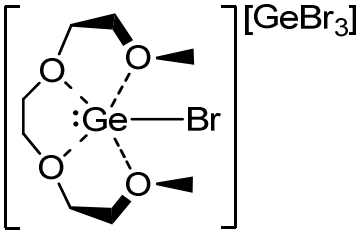

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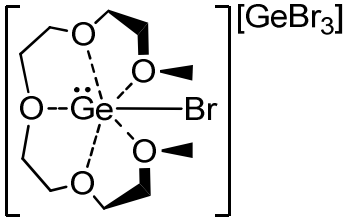
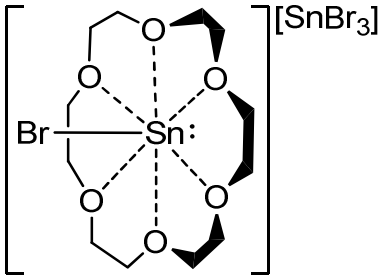


2.6$[GeBr_3]$

Chapter 3



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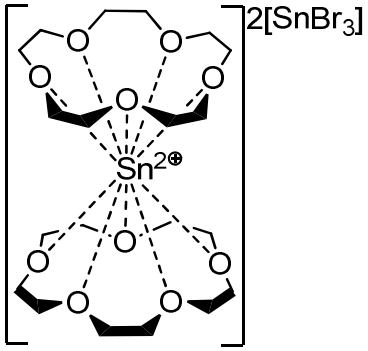

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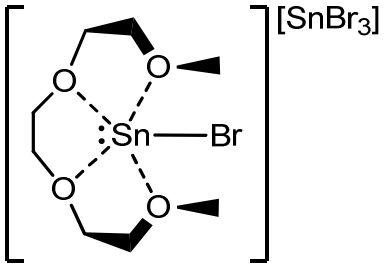

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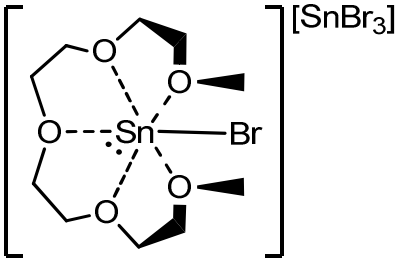

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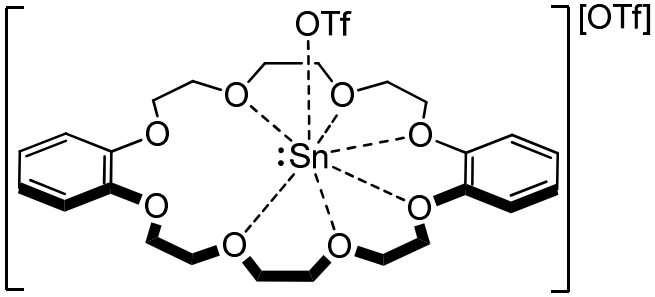
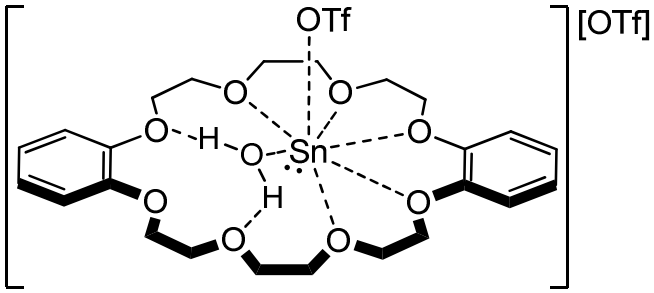


3.5[OTf]



[**3.5**(H_2O)][OTf]

Chapter 1: Introduction to the Chemistry of Polyether Complexes of Heavier Main Group Elements in Low Oxidation State

1.1 Introduction

In this first chapter, the chemistry of polyether ligands including crown ethers, glymes and related ligands with main group elements – particularly with heavier group 13 and 14 elements, and the progress made over the past decades are explored. A review of important and related concepts such as valence and oxidation state and of the chemistry of group 14 elements, especially in lower oxidation states is also included in this chapter.

Ligands such as crown ethers and cryptands are a very interesting class of complexing ligands due to their remarkable binding ability. This special ability of these interesting ligands was initially exploited for binding metal ions – especially those from the s-block.[1] In the p-block[2], the first reported examples of crown ether complexes with metallic cations included aluminum,[3] gallium,[4] indium,[4–7] thallium,[8] tin,[9] lead,[2] and bismuth.[2]

As mentioned above, crown ethers and cryptands have strong ligating properties towards metal cations. In recent years, there has been substantial interest in stabilizing group 13 and 14 elements in lower-than-usual oxidation states using crown ethers and their related ligands. The first cryptand-encapsulated germanium(II) dication synthesized by the Baines group in 2008 paved the path for the isolation of many other polyether complexes of germanium(II) in the following years.[10]

The Macdonald Group, our research group, in collaboration with other groups, has demonstrated that the properties of crown ethers and of the more flexible glyme ligands make them ideal for the stabilization of low-valent group 13 and 14 elements.[6,10,11]

1.2 Crown ethers and related ligands

1.2.1 Names and Structures

Crown ethers are heterocycles containing repeating ethyleneoxy, (-CH_2CH_2O-) units. They have a general name of [x]crown-y where x is the number of atoms in the ring and y is the number of oxygen atoms within that same ring. The smallest value of y is 2, as in [6]crown-2 (1,4-dioxane). The repeating ethyleneoxy units are two in 1,4-dioxane, while [18]crown-6 has six such units.[12] They are well known as "crowns" rather than their systematic names (e.g.[18]crown-6 is 1,4,7,10,13,16-hexaoxacyclooctadecane) because of their conformation and their peculiar property of binding with cations. The first cyclic polyether dibenzo[18]crown-6 synthesized by Pedersen in 1967, was called by him "the crown" because of the appearance of its molecular model and its ability to crown the cations.[13] Also, the term "coronands" was coined for crown ethers and "coronates" for their complexes.[14] Four different crown ethers are used in this thesis to synthesize the new polyether complexes of group 14 cations. The structures of these four crown ethers are depicted in **Figure 1.1**, along with the structure of a common cryptand, which is close relative of the crown ethers.

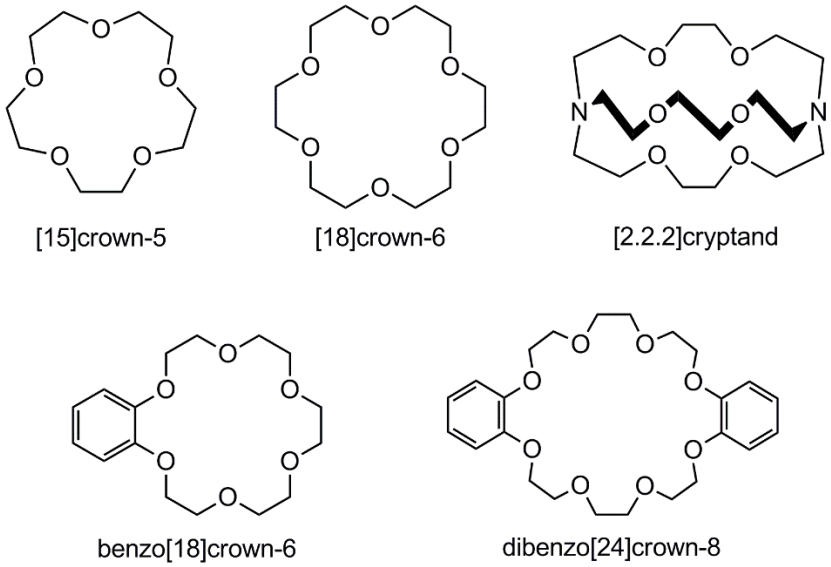


Figure 1.1 Examples of crown ethers and cryptand

The cryptands were first synthesized by Lehn.[15] He designed these ligands as a three-dimensional analogue to the crown ethers and named them "cryptands" from the Greek word "kruptos" which means "hidden" to express their special topological shape. The most common ligand of this series is cryptand[2.2.2], similar in size to the [18]crown-6. The numbers [2.2.2] indicate the number of oxygen atoms in each of the three bridges as shown in **Figure 1.1**. The presence of the third chain that converts the "two-dimensional" crown ethers into a three-dimensional ligand system is the major difference between crowns and cryptands. [18]crown-6 and cryptand[2.2.2] are representative of each group.

Acyclic crown ethers are called "podands"(open-chain crown type compounds)[14] and their complexes "podates". Examples of podands are the so-called "glymes".[14] Similar to crown ethers and cryptands, the naming of glymes is based on the number of oxygen atoms present but it must be noted that there is always one more oxygen atom present than

suggested by the numerical prefix. For example, the triglyme has 4 oxygen atoms and the tetraglyme has 5 oxygen atoms. These two common glymes are used in this thesis and their new complexes with cations of group 14 elements are characterized in the following chapters. The structures of these two types of glymes are given in **Figure 1.2** below.

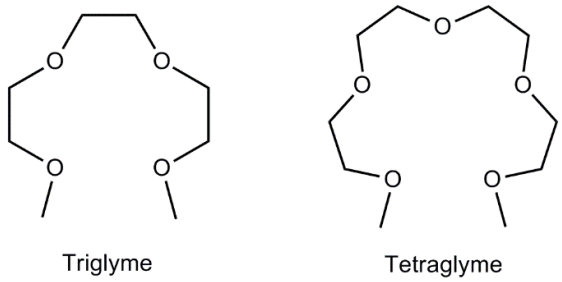


Figure 1.2 Examples of glymes

1.2.2 A brief overview of history, properties and applications of crown ethers

In 1913, Alfred Werner won the Nobel Prize for discovering that neutral ligands are able to ‘‘coordinate’’ with metal ions.[16] In 1967, after half a century, Pedersen discovered the crown ethers and examined their abilities to bind strongly with metal ions. Since then, the study of crown ethers and their related ligands has grown at an incredible pace.[13,17]

Many different types of crown ethers (crown ether diesters, azacrown ethers, thiacrown ethers, etc.) have been synthesized and reported over time.[18] Their binding selectivity and strength toward a wide range of metal ions, nonmetal ions, and neutral molecules have been investigated. The study of crown ethers and their strong binding abilities has considerably contributed to the development of host-guest chemistry and the emergence of supramolecular chemistry.[18,19] In 1987, the Nobel Prize was awarded to

recognize three chemists, Pedersen,[20] Cram,[21]and Lehn,[22] for their remarkable work in host-guest and supramolecular chemistry.

When Pedersen wanted to synthesize a new complexing agent for divalent cations, he used catechol (1,2- dihydroxybenzene) as the key element.[23] The strategy was to use one of the two hydroxyl groups to connect to a linker and attach to a second catechol. He obtained the desired product and also a neutral material, which appeared to interact with metal cations even though the compound was uncharged.[24] The unexpected product was the dibenzo[18]crown-6 (**Figure 1.3**)[13], one of the most common crown ethers now. The formation of the crown ether, as the unexpected product of the synthesis reaction, was a consequence of the presence of an alkali metal-containing base (such as NaOH).[13] Pedersen earned the Nobel Prize for his remarkable discovery of crown ethers. This example of a cyclic polyether with special complexing abilities first recognized by Pedersen became the origin from which the field of supramolecular chemistry developed.

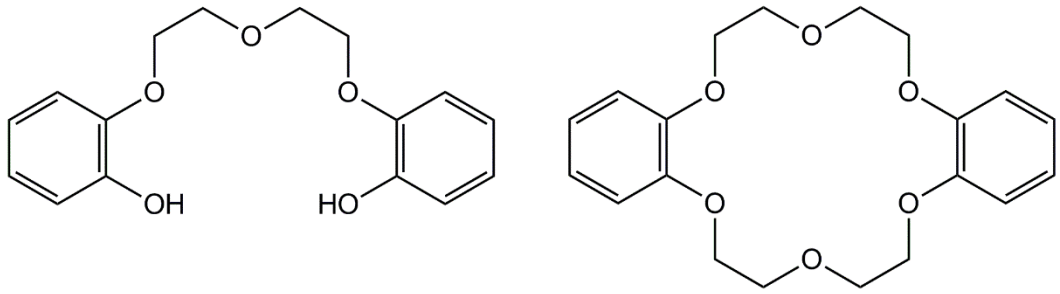


Figure 1.3 Products synthesized by Pedersen

Crown ethers containing a ring of six oxygen atoms, exemplified by [18]crown-6 and benzo[18]crown-6 (depicted in **Figure 1.1**) are the strongest and most versatile complexing agents. The hole diameter of 4 Å of the first synthesized crown ether with a six

oxygen ring, dibenzo[18]crown-6, is large enough to accommodate any unsolvated metal cation. It is noteworthy that the ammonium ion forms a complex with this crown ether[13] and since the ligand is neutral, the cation complex must be always associated with an anion.

There are more than 300 complexes of only dibenzo[18]crown-6 reported in the Cambridge Structural Database since Pedersen's first discovery. A stunning amount of new structural types and new compounds were prepared and reported in the literature.[25,26] Many hundreds of structures are now known and they differ in many ways, including conformations and metal-donor distances.

The most common compounds in the [3n]crown-n family (e.g. [12]crown-4, [15]crown-5, [18]crown-6, [21]crown-7 and [24]crown-8) are well known for complexing alkali metal cations, such as Li^+, Na^+, K^+, and Cs^+. [18]crown-6 is the superior binder in all of the cases. The strengths of binding for these compounds vary, according to the relationship between the size of the ring and cation or to the associated counter-anion, and depending on the solvent used in the complexation reaction, too. It is worth mentioning that the fusion of a benzene group to [18]crown-6 as in the cases of both benzo[18]crown-6 and dibenzo[18]crown-6 caused reduction of the binding strength.[27]

According to the initial understanding of the concept of so called ''hole-size relationship'' in the case of simple macrocycles, binding is best when there is a close or exact size correspondence between the cavity size of the ligand and the metal cation. In general, a good correspondence between these two is a good strategy if the cation will be held by a relatively rigid scaffold.[27] The modern understanding of this concept has somewhat modified the simple "hole-size" idea, particularly because of the flexibility of

the crown ethers. All the binding constants peaks for [18]crown-6 when it binds with Na^+, K^+, NH_4^+, and Ca^{2+} show maximum values for this crown (compared with other common crowns from [12]crown-4 to [24]crown-8). When [18]crown-6 binds the K^+ ion (**Figure 1.5**), the size fit is good, the ethylene units are not conformationally compromised, and the six donor groups are focused on the cation with three oxygens above the plane and three below.[27] It is also well known that [18]crown-6 has a high affinity for the hydronium ion $H_3O^+$and NH_4^+ , as they can fit inside the crown ether (**Figure 1.4**).

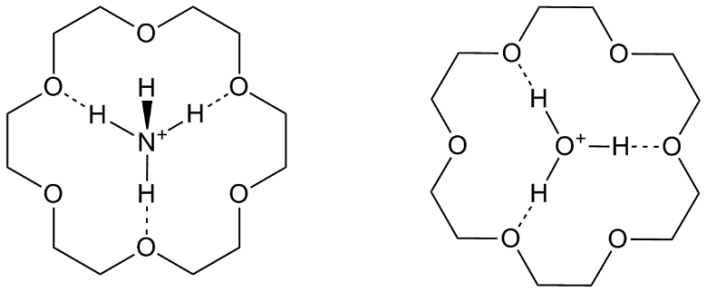


Figure 1.4 Complexes of [18]crown-6 with H_3O^+ and NH_4^+

When the crown ether is smaller than the target cation, a sandwich structure may form rather than a simple 1:1 complex. The cation is sandwiched between the two rings of the crown ether (**Figure 1.5**).[28]

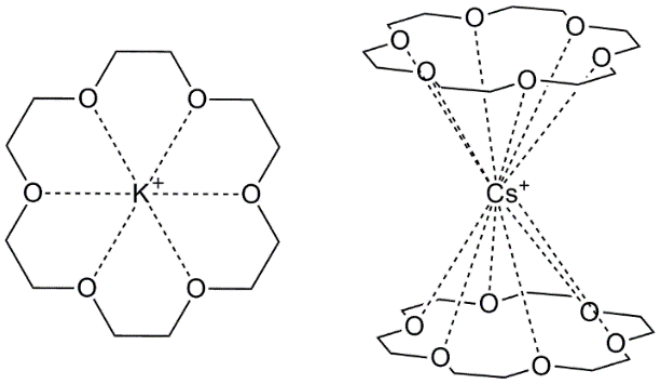


Figure 1.5 Complexes of [18]crown-6 with K^+ and Cs^+

An impressive number of coordination complexes with many types of metal ions has been reported since the discovery of crown ethers. Given the above examples of complexes of crown ethers with s-block elements, at this point, it is worth emphasising that for most of polyether complexes of p-block elements – particularly the elements at left-hand side (group 13 and 14), the cation is in a lower-than-usual oxidation state. An element in lower oxidation state is more electron rich and less electronegative than it is in the usual oxidation state, thus these elements, especially the heavier elements of groups 13 and 14 behave more like s-block metals, having lower ionization energies and electron afinities.[29] Also, generally the estimations of the cavity sizes of common crown ethers used to bind p-block elements have been based on the studies previously done with s-block metal ions.[29]

Since Pedersen's fortuitous discovery of crown ethers, studies over the past decades have demonstrated that crown ethers can play interesting roles in many chemical and physical processes. As previously described, the special characteristics of crown ethers are their strong binding ability and high selectivity for metal ions. They have a very important role in ''host–guest'' chemistry; the crown ether plays the "host" molecule, which has the ability to encapsulate a "guest" molecule (e.g. a metal cation) via non-covalent interactions. Crown ethers have many useful applications based on their high selectivity for metal cations of different sizes. Their capability of enclosing NH_4^+ is of special importance considering the fundamental role of the ammonium ion in biological processes. The wide range of their applications includes analytical chemistry, organic synthesis, solvent extraction, phase transfer catalysis, biochemical modelling, preparation of Zintl salts and stabilization of various elements in lower than their usual oxidation state. The focus of this

thesis is stabilization of low oxidation state germanium and tin by crown ethers and related glymes.

1.3 Oxidation state and related concepts

1.3.1 Definitions and relationship of common terms

It is worth clarifying the notions of valence, oxidation state and coordination number, terms often used in this thesis and describe their relationship. Each of these terms has individual meaning. Valence is defined as "the number of electrons that an atom uses in bonding".[30] Oxidation state sometimes referred to as oxidation number is "the charge remaining on an atom when all ligands are removed heterolytically in their closed form, with the electrons being transferred to the more electronegative partner".[30] Coordination number is defined as "the number of atoms bonded to the atom of interest".[30] These are simple definitions of three related but fundamentally different concepts.

The valence of an atom in a molecule is calculated as the difference between the number of electrons in valence shell of the free atom (group valence) and the number of nonbonding electrons on the atom in the molecule. According to this mathematical method, it becomes evident that the valence of an atom cannot be calculated only from the empirical formula of its compounds.[30] The valence state indicates how many electrons an atom has used in bonding, according to Sidgwick's simplest definition. This knowledge is very important because it provides information about the properties of a molecule. As an example, when the valence of an atom is less than the group valence, it indicates that there are non-bonding electrons on the atom, which means the atom is capable to form new

bonds. For example, the nitrogen in NH_3 is trivalent, which indicates that there is a lone pair of electrons on nitrogen that may be used to coordinate additional groups such as H^+. Definitely, the valence concept provides useful information about the nature (structure, bonding and reactivity) of a molecule.[30]

Although, there are many situations when, by coincidence, the valence of an atom in a molecule is equal to its oxidation state, the two concepts are different.[30] For example: C is tetravalent but has an oxidation state of 0 in Me_4C, or N is pentavalent but has an oxidation state of -3 in $[NH_4]^+$. There are different ways to assign the oxidation state of an atom. In contrast to valence state, oxidation state of an atom in a molecule can be calculated from the molecular formula. Chemists use a set of axioms or guidelines for assigning the oxidation numbers[31] (e.g. hydrogen is assigned an oxidation number of +1; oxygen is assigned an oxidation number of -2) to determine the oxidation state of an atom in a compound. These conventional rules are useful for balancing redox reactions.

For p-block elements the conventional methods of assigning the oxidation state can often be ambiguous or misleading. For example, the formal oxidation state determined by using the axioms does not provide information about the actual distribution of electrons within the molecule, as these rules are based on relative electronegativities of the atoms in the molecule. For this reason, the alternative model used by our research group is based on the number of non-bonding electrons of the atom within the molecule and on the assumption that the atom of interest must be considered less electronegative than any bonded atoms. Although this assumption is unrealistic, the alternative model eliminates irregularities in the assignment of oxidation states and many ambiguities in the chemistry of a molecule.[32] For example, whereas the conventional rules suggest that the carbon in

Me_2CCl_2 and $:CCl_2$ has an oxidation number of +2 these molecules have very distinct chemical properties. While the carbene $:CCl_2$ exists only as a reactive intermediate, Me_2CCl_2 is known as a stable compound.[30] According to the alternative model the carbon has an oxidation state of +4 in Me_2CCl_2 and +2 oxidation state in $:CCl_2$ which explain the different chemistry of these two compounds.

Applying the alternative method to group 14 elements, the oxidation number of +4 is assigned to an atom with zero non-bonding electrons. The next oxidation numbers of +3, +2, +1, 0 are assigned to atoms with one, two, three and four accordingly, as illustrated in **Figure 1.6**. This alternative approach relates more closely to the valence concept described above, than to the conventional method of assigning oxidation states which provides little insight into the nature of a molecule.

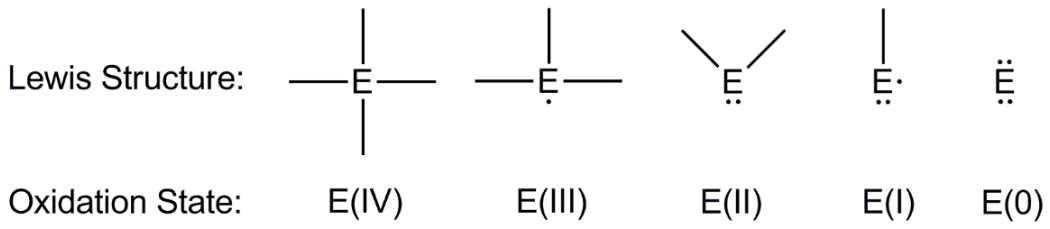


Figure 1.6 Oxidation states of Group 14 elements (E) based on the alternative model

The relationship between the valence and the coordination number is also worth mentioning. Defined as the number of atoms attached to the atom of interest, for neutral molecules of the hydride type, AH_n as an example, n, the coordination number of an atom A, is equal to its valence. In the case of a dative covalent bond (donor–acceptor bond), the relationship changes. In this case one of the atoms provides both electrons and the coordination number and the valence are not equivalent. Coordination of a dative ligand

(donor, such as H_2O or NH_3) to an atom A (acceptor) does not require any electrons from A and as a consequence the valence of A remains unchanged upon coordination of the ligand.[30] The coordination number of an atom is sometimes confused with its oxidation state.

1.3.2 Oxidation states of Group 13 and 14 Elements

Chemists used the idea of an element existing in a particular oxidation state to explain the structural characteristics and chemical behavior of a molecule containing that element. By definition, an element in a lower oxidation state is more electron-rich than it would be in a higher oxidation state, and the presence of these additional electrons can affect considerably the chemistry of compounds containing these elements.[33,34] The presence of an element with either an unusual formal oxidation state or valence state in a compound can suggest interesting structural or chemical features and both concepts should be considered. For the main group elements, the relative stability of lower oxidation and valence states within a given group tends to increase as the atomic number increases.[33]

For the majority of group 13 elements, the +3 oxidation state (E^{III}, E = B, Al, Ga, In) is the most stable state. This explains the Lewis-acidic behavior of the electron deficient neutral molecules containing these elements. The compounds containing a group 13 element in the low +1 oxidation state (E^{I}) can behave either as Lewis bases or Lewis acids (**Figure 1.7**).[6]

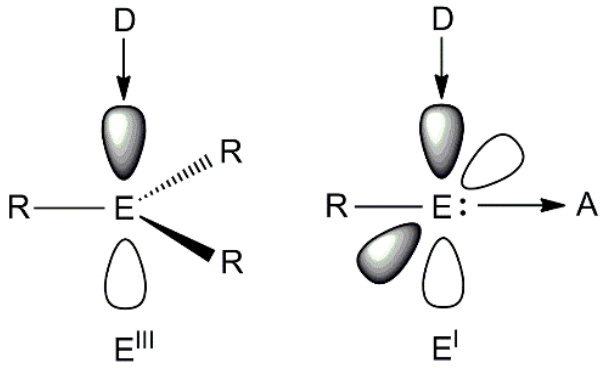


Figure 1.7 Group 13 elements (E) in the +3 and +1 oxidation states with electron donors (D) or acceptors (A)

The investigation of main group elements in unusually low oxidation states has been a very active area of research since the 1990s. As mentioned in the introduction, reported examples of crown ether complexes with cations of group 13 elements include aluminum, gallium, indium and thallium. Earlier members of our group have demonstrated that In(I) centres that are usually unstable can be stabilized using two different crown ethers.[6] These indium complexes are presented in Section 1.5 of this chapter.

For the group 14 elements, there are two common oxidation states: +2 and +4. For carbon, silicon, and germanium the +4 oxidation state is more common and the heavier tin and lead are more stable in the +2 oxidation state. In the +2 oxidation state, the element has two non-bonding valence electrons. The stability of the lower oxidation state increases as the atomic number increases down the group, and the increasing stability is attributable to the inert pair effect.[33] In this thesis, complexes of germanium and tin in the +2 oxidation state are the primary focus and their chemistry is discussed in the next two sections.

1.4 Group 14 Elements and the Chemistry of Ge(II) and Sn(II) Compounds

1.4.1 Group 14 Elements

Group 14, sometimes called the Carbon Group (or the tetrels), consists of C, Si, Ge, Sn and Pb and thus includes elements with properties that range from non-metallic to metallic. Carbon, the lightest element, is a true non-metal, followed by silicon and germanium, the two metalloids. The heavier elements tin and lead are both metals. Germanium, tin and lead belong to the silicon subgroup and they are called the heavy elements of Group 14. Germanium and tin are the elements of focus in this thesis.

The electron configuration of group 14 elements is: [core]ns^2np^2, where n is the period number (or principal quantum number); due to the number of valence electrons these elements are known as "tetrels" (from the Greek word *tetra*, which means *four)*.

In the past few decades, the chemistry of the heavier Group 14 elements - particularly in lower oxidation states, has become a field of great interest. An element in lower oxidation state has more valence electrons than in the higher oxidation state. The valence electrons for main group elements are found in VSEPR-active s and p orbitals. The compounds containing lower than usual oxidation state elements are more reactive than their relatives in the usual oxidation state, since these elements tend to be coordinatively unsaturated and have electrons available.[34] The structures and reactivities of their compounds are considerably compared to those of their carbon congeners.[35,36,37,38]

1.4.2 Metallylenes

Metallylenes – the compounds of heavier group 14 elements in low oxidation state, are considered among the most studied analogues of carbenes.[39,40,41] Generally, they are represented as: R_2M or ER_2, (M or E = Si, Ge, Sn, Pb), where R can be, for example, simple alkyl or aryl substituents or a group bound through a heteroatom (O, S, or N). Silylenes, germylenes, stannylenes and plumbylenes are divalent species with a +2 oxidation state.[42]

Arduengo and co-workers isolated and characterized the first stable N-heterocyclic carbene (NHC).[43] N-heterocyclic carbenes are cyclic carbenes in which the divalent carbon atom is flanked by two nitrogen atoms; these two atoms donate electron density into the vacant p-orbital of carbon, thermodynamicaly stabilizing the system.[44] Analogs of NHC with heavier group 14 elements such as Si,[45] Ge,[46] and Sn[47] were synthesized and reported over the years.

At this point, comparing the ground states of metallylenes and carbenes is important for a better understanding of the chemistry regarding these compounds. While the carbenes can have a singlet or triplet ground state, their heavier analogs have a single state (since two valence electrons remain as a singlet pair in the ns orbital of the metallylene)[48]. In **Figure 1.8** only the triplet ground state of carbene is depicted for comparison with the singlet ground state of a metallylene.

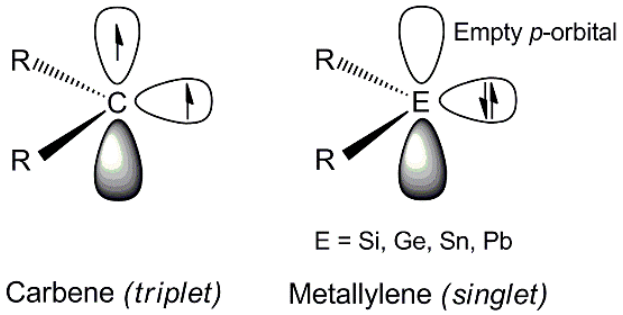


Figure 1.8 Difference between the ground states of carbenes and metallylenes.

The high reactivity of metallylene is due to their empty p-orbitals and in order to stabilize and isolate the reactive metallylenes kinetic and/or thermodynamic (or electronic) stabilization is required. The electronic stabilization involves the transfer of electron density from a non-bonding electron or π donor ligands to the vacant p-orbital of E (Si, Ge, Sn, Pb). This type of stabilization can be accomplished in three different ways: π-donation from an intramolecular donor (1), σ-donation from an intermolecular (2) or intramolecular donor (3) as illustrated in **Figure 1.9**.[42,48]

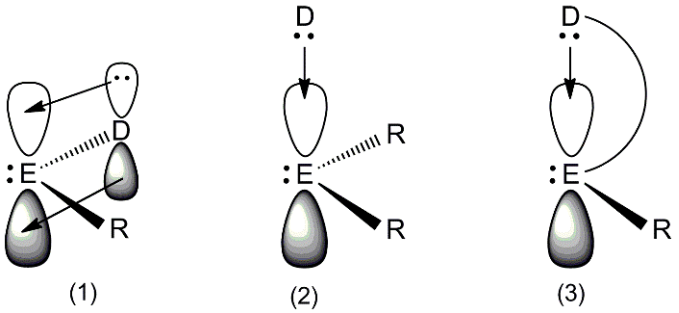


Figure 1.9 Ways of thermodynamic stabilization of metallylenes

The use of bulky alkyl or aryl substituents (R), which will suppress self-oligomerization of metallylene and prevent nucleophilic attack on their empty p-orbital, is a good example of providing kinetic stability **(Figure 1.10)**.[5]

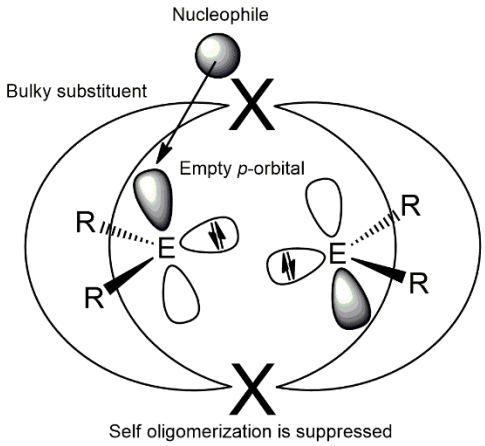


Figure 1.10 Kinetic stabilization of metallylenes using bulky substituents (E=Si, Ge, Sn, Pb)

1.4.3 Germylenes and Stannylenes

The chemistry of both germanium(II) and tin(II) is rich and diverse. A variety of substituents or ligands have been employed utilizing kinetic and thermodynamic stabilization resulting in new and unique structures. A brief review of some examples of the various ligands used and the resulting complexes is provided in the last part of this section.

In comparison to their analogues carbenes and silylenes,[47]germylenes are less reactive, because of the larger energy gap between the s-orbitals and p-orbitals of germanium.[49,50] Lappert et al. reported in 1974 the first stable acyclic diamidogermylene $[(Me_3Si)_2N]_2Ge$.[51] An example of one of Lappert's germylene ($Ge[CH(SiMe_3)_2]_2$), which exists as a dimer in the solid state, is shown in **Figure 1.11**.[52] Later, Jutzi et al. isolated the germylene $[(Me_3Si)_3C][(Me_3Si)_2CH]Ge$ by replacing one of the $CH(SiMe_3)_2$ groups with $C(SiMe_3)_3$, and characterized it crystallographically in 1991. This was the first monomer stable in solution and solid state.[53]

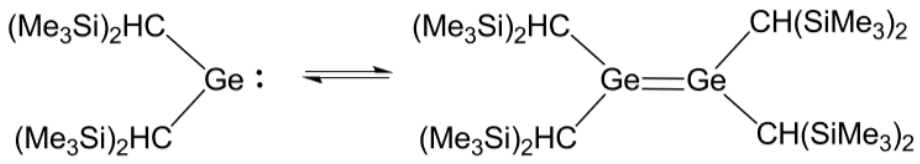
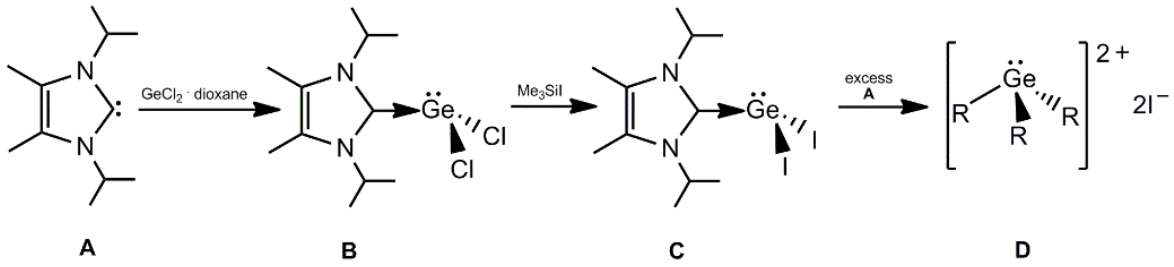


Figure 1.11 Example of Lappert's germylene complexes in monomeric and dimeric forms

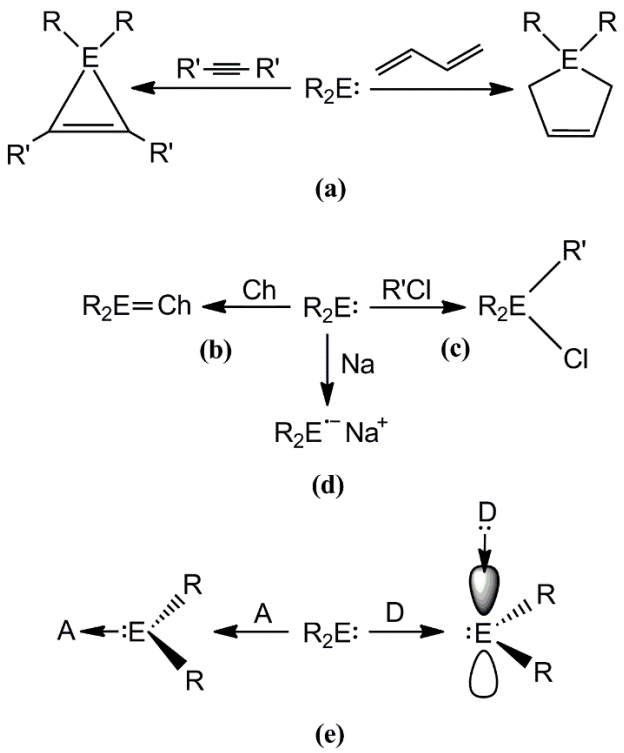
Different types of germylene derivatives[54] have been reported and reviewed periodically.[55,56] In 2007, Baines and co-workers reported a dicationic complex of germanium coordinated by three N-heterocyclic carbene ligands.[57] In this case, the strong donor ability of NHCs enabled the synthesis of this new Ge(II) complex. This research group have also synthesized two carbene-dihalogermylene complexes B and C (halogens= Cl, I), explored their reactivity with carbene A (^{i}Pr NHC) and prepared the diiodide salt D, which has three identical carbenes bonded to the germanium center (**Scheme 1.1**).[57]



Scheme 1.1 Synthesis of the dicationic complex of germanium (R= ^{i}Pr NHC)

Generally, the chemistry of metallylenes can be divided into four different classes of reactions such as: cycloaddition (e.g. interaction with alkynes result in [2+2] cycloadducts and interaction with butadienes give [2+4] cycloadducts)[58–60] (a), chalcogenation (the reaction with elemental chalcogens, Ch = O, S, Se, Te, to form the corresponding "heavy ketone" analogues R_2E=Ch)[61,62](b), insertion (reaction of insertion

of ER_2 into haloalkanes to form $R_2ER'X$, X = halogen)[37,63–65] (c), and reduction (ER_2 can accept an electron into the empty p-orbital of E to give radical anions)[66] (d). In the majority of the reactions involving germylenes and stannylenes, nucleophilic attack on the vacant p-orbital of Ge or Sn results in the formation of two new bonds at the new Ge(IV) or Sn(IV) centre. Germylenes and stannylenes can also form donor-acceptor complexes acting as donors or acceptors[67,68] (**Scheme 1.2**).[42,48,69]



Scheme 1.2 Reactivity of germylenes and stannylenes (E = Ge, Sn)

It has already been demonstrated that, by using different categories of ligands or substituents, stabilization (steric and/or electronic) of group 14 elements in low oxidation state can be accomplished. It is important to emphasize at this point that, for example, the introduction of a donor D (a Lewis base) has produced stable donor-acceptor complexes. The transfer of electron density from the base into the empty p-orbital on tetral (E)

(illustrated in **Scheme 1.2**, **e**) reduces the electron-deficiency of the system and moderates the reactivity of the metallylene. When E=Ge (germylene) the donor D = ether, imine, phosphine or carbene.

The perfect example of such donor-acceptor complexes is the NHC- dimesitylgermylene complex (NHC-Ge(Mes)$_2$ where Mes = 2,4,6-trimethylphenyl) synthesised and characterizated by Baines group and this was the first example of base stabilization of a highly reactive :GeR$_2$ species by a carbene.[67]

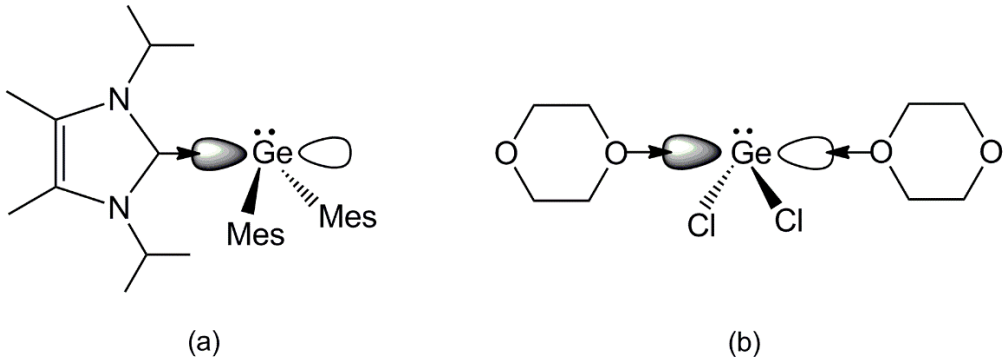


Figure 1.12 (a) Structure of NHC-Ge(Mes)$_2$ and (b) Structure of GeCl$_2$(1,4-dioxane)

A very good example of an intermolecular stabilization of a germylene is GeCl$_2$(1,4-dioxane), illustrated in **Figure 1.12**, a stable inorganic germanium(II) derivative and a versatile reagent used for preparation of many germanium compounds.[67] In fact, dihalogermylenes GeX$_2$ were the first known and studied divalent germanium species.[42] The structure of the well-known germanium dichloride complex consists of infinite chains of alternating GeCl$_2$ and 1,4-dioxane molecules. The coordination number of the Ge(II) is four (with two covalent bonds to two Cl and two weak bonds to two O from two dioxane molecules).[70] GeCl$_2$(1,4-dioxane) was first synthesized and structurally characterized in the early 1970s.[49]

It is believed that stannylenes SnR_2 belong to the first organotin compounds ever prepared, more than 150 years ago. In those days short-lived intermediates of high reactivity were not known.[71] The chemistry of stannylenes has been of much interest in the last four decades. The first stable dialkylstannylene in solution was isolated by Lappert and co-workers in 1976, the same group that prepared the germylene analogues. As illustrated in **Figure 1.13,** this dialkylstannylene exists as a monomer–dimer equilibrium mixture with the dimer called "a distannene"; there are many examples of distannenes that exist in the crystalline state and dissociate to form stannylenes in solution.[72–74]

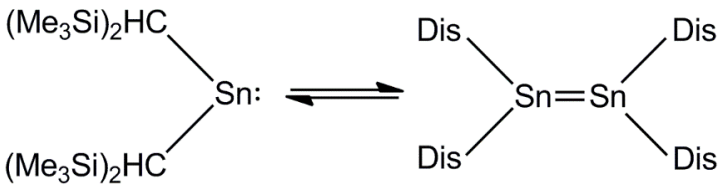
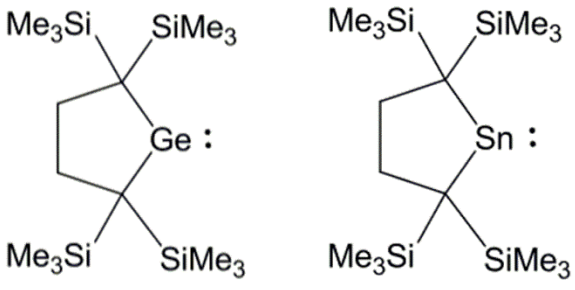


Figure 1.13 Lappert's dialkylstannylene complexes in monomeric and dimeric forms

Kira et al. used a bidentate ligand to stabilize a dialkylgermylene (analogues to Lappert's original germylene) and to isolate the first stable dialkystannylene in its solid state (**Figure 1.14**).[75,76]



(a) (b)

Figure 1.14 (a) Kira's cyclic dialkylgermylene and (b) dialkylstannylene

A variety of stable monomeric germylenes[61,77–79] and stannylenes[72,73,80,81] were isolated by substitution of various substituents with bulky aryl groups. Some of these examples are depicted in the figure below.

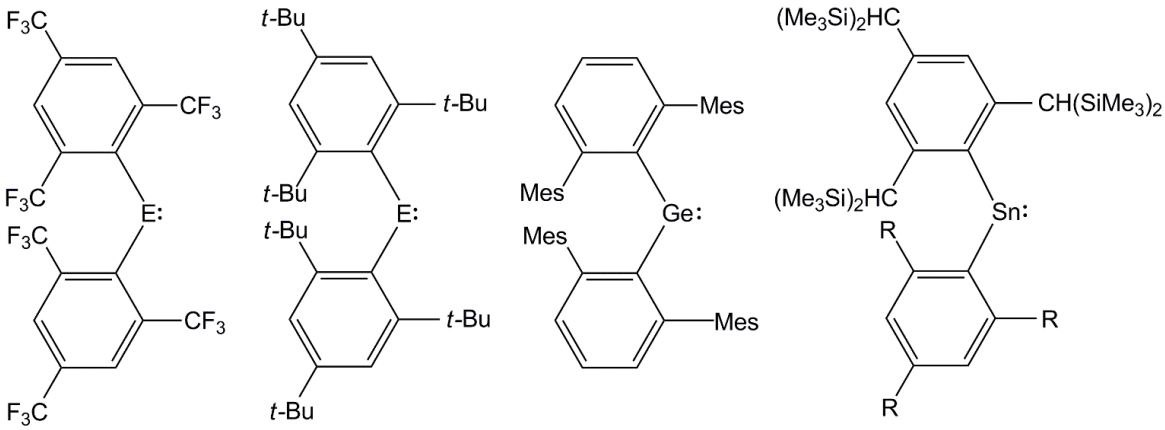
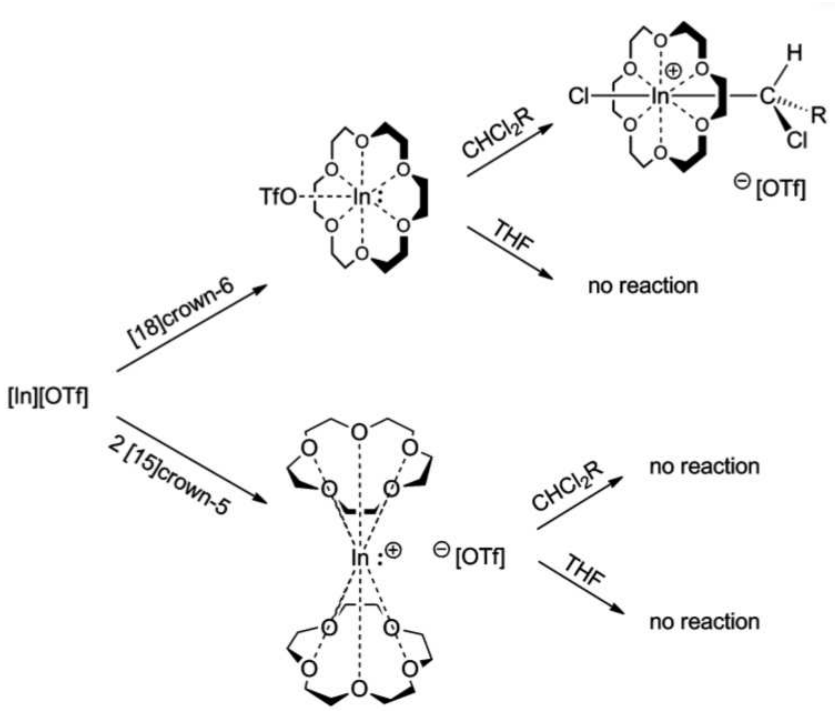


Figure 1.15 Examples of stable monomeric germylenes and stannylenes with bulky aryl groups (E= Ge, Sn; Mes = 2,4,6-trimethylphenyl ; R= ^{i}Pr, cyclohexyl, 1-ethylpropyl)

1.5 Macrocyclic Polyether Ge and Sn Complexes

Cyclic polyethers, such as crown ethers and related ligands, have been used to complex metal cations across the entire periodic table. Polyethers have been known for their ability to complex tin and lead in the +2 oxidation state. In the last decade, it has been demonstrated that the multiple weak donor-acceptor interactions with heteroatoms of the polyethers can stabilize germanium and silicon and the first example of a germanium(II) dication encapsulated within a cryptand was reported during this period of time.[82] In the same time frame, our research group has investigated the use of crown ethers and glymes ligands for stabilization of low oxidation state group 13 and 14 elements. For the group 13 elements, the work of our group has focussed on stabilizing indium in the low oxidation state +1. In(I) complexes with two differently sized crown ethers, such as [15]crown-5 and

[18]crown-6, were synthesized, characterized and their reactivity investigated. The characterization methods indicate the formation of the two salts of indium(I): [In([15]crown-5)$_2$][OTf], containing the sandwich-like cation, and [In([18]crown-6)][OTf], (OTf = $CF_3SO_3^-$), with unique structures and different reactivities (**Scheme 1.3**).[11]



Scheme 1.3 Synthesis and reactivity of In(I) complexes[11]

Similar results were expected for germanium and tin with the same crown ethers considering that In(I) is isovalent with Ge(II) and has the same electronic structure as Sn(II). The work of a few research groups, including ours in the past decade, was summarised, and various examples of crown ethers and cryptand complexes with Ge(II) and Sn(II) are depicted in **Figure 1.16**.[10,11,57,82] An overview of the chemistry of these complexes is given in this last section of the chapter.

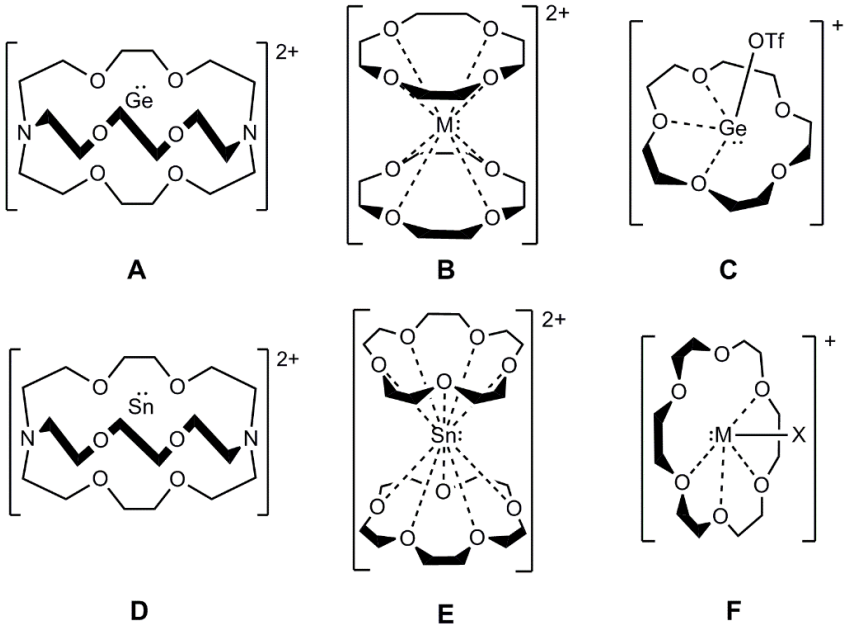
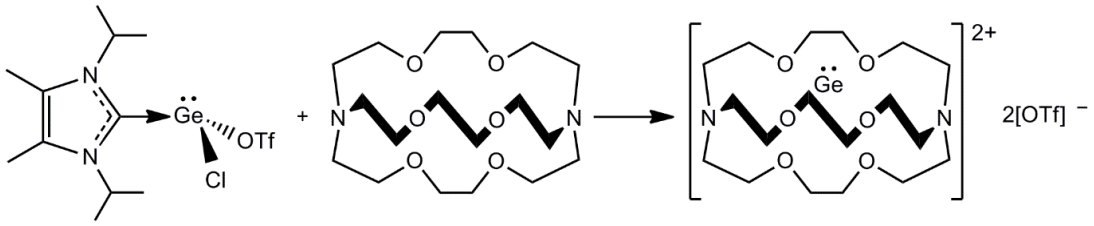


Figure1.16 Macrocyclic Polyether Ge and Sn Complexes (M=Ge; X=Cl and M=Sn; X=Cl, OTf)

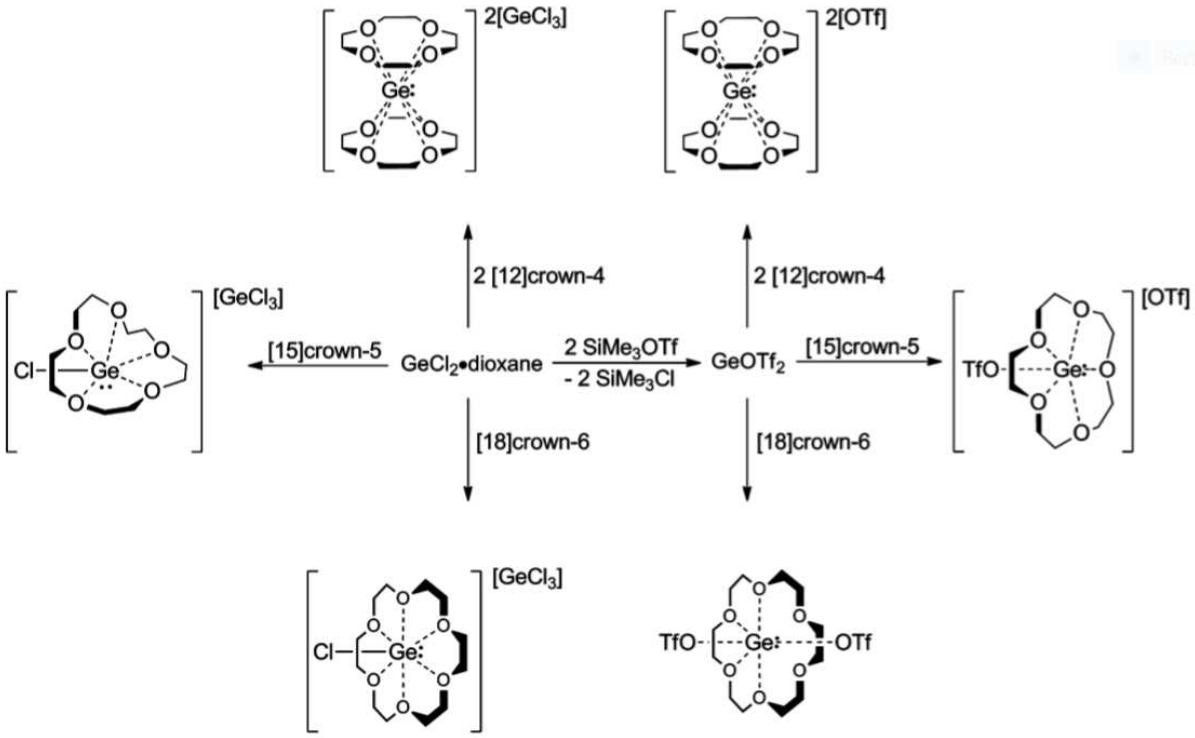
1.5.1. Cationic crown ether and related complexes of germanium(II)

The first example of a germanium dication stabilized by the [2.2.2]cryptand ligand, synthesized by Baines and co-workers (**Scheme 1.4**)[80], highlighted the possibility of isolating reactive Ge^{2+} using electron-rich macrocyclic polyether molecules to stabilize the cation with numerous weak donor acceptor interactions.



Scheme 1.4 Synthesis of complex of Ge^{2+} with the [2.2.2]cryptand

The Macdonald group, in collaboration with the Baines group and in the same time with the Reid group, demonstrated that crown ethers are also appropriate ligands for the stabilization of reactive Ge(II) dications. Three differently sized crown ethers, [12]crown-4, [15]crown-5 and [18]crown-6 were used and their unique complexes with cationic Ge(II) have been structurally characterized.[10] As with the indium complexes with crown ethers, the germanium complexes exhibit different structures depending on the size of the crown ether cavity and the ionic radius of the cation and their relationship. As a consequence of this, the first structure exhibits two [12]crown-4 molecules sandwiching the germanium dication and two counteranions $[GeCl_3]^-$ separated from Ge^{2+} (**Scheme 1.5**). In this case, the Ge^{2+} ion is too large to fit into the cavity of the crown ether. This structure is related to that of Ge(II) with the cryptand[2.2.2], illustrated earlier in **Scheme 1.4**, which contain an uncommon eight-coordinate germanium center (usual coordination numbers are two to four for Ge(II) species).[10] The crystallographic analysis indicates that the structure of $[Ge([12]crown\text{-}4)_2][OTf]_2$, ($OTf = CF_3SO_3^-$), the second complex of [12]crown-4 with Ge^{2+}, is similar to the first structure of $[Ge([12]crown\text{-}4)_2][GeCl_3]_2$ (both are illustrated in the following scheme).



Scheme 1.5 Syntheses of cationic crown ether complexes of Ge(II)[11]

The use of the larger crown ether [15]crown-5 resulted in the formation of two structures with different conformations. $[Ge([15]crown\text{-}5)\cdot OTf]^+$ exhibits the crown ether with a typical planar conformation and $[GeCl([15]crown\text{-}5)]^+$ features a "folded" structure of the crown; in this unique conformation the plane defined by the central germanium and three of the oxygen atoms is almost perpendicular to the plane defined by Ge and the two remaining O atoms (**Scheme 1.5**).[11]

The last two complexes of Ge(II) with the [18]crown-6 also adopt interesting and anticipated conformations considering the size of this crown ether. In both of these structures, the germanium atom is offset from the centroid of the oxygen atoms in the crown as a consequence of the larger cavity size of the crown. Especially, the structure of

[Ge(OTf)$_2$([18]crown-6)] shows a symmetrical Ge(OTf)$_2$ fragment located within the cavity of the crown (**Scheme1.5**).[10]

1.5.2 Cationic crown ether and related complexes of tin(II)

After the first crown ether complexes of tin(II) were studied in the group of Herber[83,84], complexes of tin(II) halides with [18]crown-6 and [15]crown-5 were structurally characterized by Nicholson and co-workers (**Figure 1.16, E** and **F**).[9,82,85] In 2009, our research group reported the synthesis and structural characterization of tin(II) complexes of [12]crown-4, [15]crown-5 and [18]crown-6[86] with the triflate ion (OTf^-) and tin(II) glyme complexes[11] with the same counterion, two years later. After all these crown ether complexes of tin(II) have been achieved, the Baines group reported the synthesis of the first tin(II) complexes with cryptand[2.2.2].[82] These novel complexes were characterised and their structural characteristics compared to those obtained with the crown ethers.

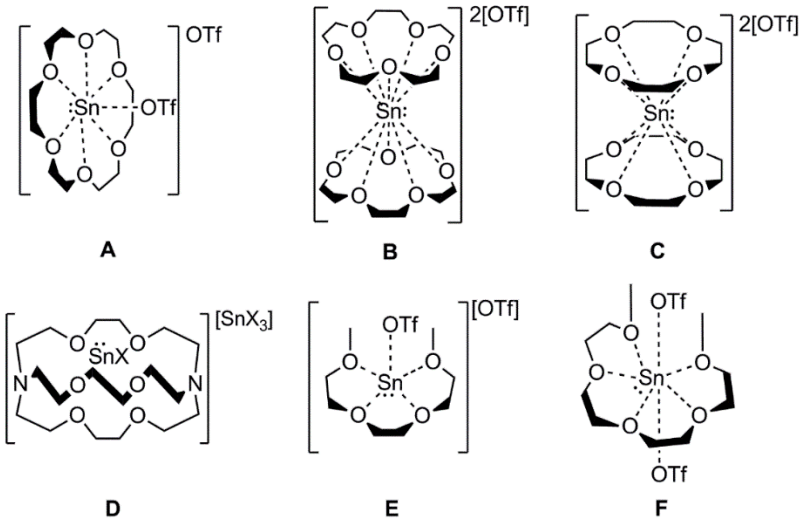


Figure 1.17 Cationic crown ether, cryptand and glyme complexes of tin(II), (X=Cl, Br, I; OTf = $CF_3SO_3^-$)

Since Sn(II) is isoelectronic with In(I) and isovalent with Ge(II), the chemistry of tin(II) crown ether complexes was expected to be similar to the chemistry of germanium(II) and indium(I) analogues. In light of the different sizes of tin(II) and germanium(II) the structure of [18]crown-6 with $Sn(OTf)_2$ (**Figure 1.17, A**) resembles the structure of [Ge([15]crown-5)OTf] and is even more closely related to the complexes of [18]crown-6 and tin halides (**Figure 1.15, F**) reported by Nicholson.[85] The smaller macrocycles, [15]crown-5 and [12]crown-4 produce 2:1 complexes. The [15]crown-5 macrocycle is too small to enclose the Sn(II) center adopting a centrosymmetric sandwich-like structure and have a stereochemically-inactive non-bonding pair of electrons (**Figure 1.17, B**).[86] The complex of [12]crown-4 and tin(II) triflate (**Figure 1.17, C**) was described as being a bent-sandwich-like structure.[86] The bent arrangement of $[Sn([12]crown\text{-}4)_2]^{+2}$ fragment is in contrast with the more conventional sandwich observed for the germanium(II) analogue $[Ge([12]crown\text{-}4)_2]^{+2}$ and have a stereochemically-active pair of non-bonding electrons.[86]

A series of cationic cryptand complexes of tin(II) halides, [Cryptand[2.2.2]SnX][SnX_3] (X = Cl, Br, I) (**Figure 1.17, D**) and tin(II) trifluoromethanesulfonate, [Cryptand[2.2.2]Sn][OTf] (**Figure 1.16, D**) were synthesized and characterised by the Baines group,[82] after they reported the first cryptand-encapsulated germanium(II) dication.[80] These new cryptand complexes were fully characterised and compared to complexes of Tin(II) halides with crown ethers. Based on the data obtained, the cryptand complexes are monocationic complexes, where the halogen atom is covalently bound to the tin atom. One of the most interesting comparisons was made between the two macrocyclic polyether complexes of tin(II) chloride with [18]crown-6 and the cryptand[2.2.2], these two being the most related ligands; it was suggested that the *s*

electron density at tin is greater and also more spherically symmetric in the cryptand complex then in the analogous crown complex. Finally, the tin chemistry was compare with the analogous germanium chemistry. While Ge(II) formed a dicationic complex with the cryptand[2.2.2] (**Figure 1.16, A**), Sn(II) produced two cryptand complexes: a monocationic complex with the halides and a dicationic tin(II) cryptand complex with triflate as the counterion, also depicted in **Figure 1.16**. The difference between the size of tin and germanium could simply explain this contrast; the larger tin favors a higher coordination number and may require a larger cryptand to be completely encapsulated.[80]

To determine if the acyclic analogues of crown ethers, the more flexible glymes, are also suitable for the stabilization of tin(II), our research group investigated a series of complexes of tin(II) triflate and two glyme ligands. Tetraglyme and triglyme were the two glymes investigated using a variety of computational and experimental methods.[11] The treatment of $Sn(OTf)_2$ with the glymes resulted in the formation of the 1:1 complexes $Sn(OTf)_2$·triglyme and $Sn(OTf)_2$·tetraglyme, (**Figure 1.17, E, F**). In both complexes the ligand binds the tin atom in a belt-like manner. In the triglyme complex, there is one triflate environment with a longer Sn−O distance and the other with a significantly shorter Sn−O distance. The first triflate anion has the characteristics of a "free" anion. For the tetraglyme complex, there is a small range of distances between the tin atom and the triflate anions.[11]

1.6 Thesis Overview

Our research group has long been interested in the synthesis of compounds containing main group elements in lower than usual oxidation states. This thesis presents the synthesis and structural characterization of new polyether complexes of germanium and tin in +2 oxidation state. Indium(I) and germanium(II) halides and triflates complexes with various polyethers, reported by earlier members of our group,[10,11] exhibit different structures depending on the relationship between the size of the crown ether cavity and the ionic radius of the cation and also on the substituents on the cation (In^{+} or Ge^{2+}). A similar chemistry was anticipated for Sn^{2+} given that Sn(II) is isoelectronic with In(I) and isovalent with Ge(II). As an extension to the previous work, the reactions between Ge(II) bromide and Sn(II) bromide with four differently sized crown ethers and two glymes are examined in detail. The complexation of Ge(II) and Sn(II) using larger crown ether ligands will also be explored. Chapter 2 presents the synthesis and structural characterization of Ge(II) bromide polyether complexes and the remarkable results of the reaction between $GeCl_2$·dioxane and dibenzo[24]crown-8 are included in this chapter. Similarly, Chapter 3 describes the synthesis and structural characterization of Sn(II) bromide with crown ether and glyme complexes and presents the synthesis of a new complex of $Sn(OTf)_2$ with dibenzo[24]crown-8 and the isolation of a new water adduct. Chapter 4 provides the conclusions as well as future work. The future work section includes the preliminary results of the investigation into the reactivity of the new polyether complexes. The reactions with ammonia and water of the new polyether complexes of germanium(II) as well as deprotonation reactions of the water adduct of Ge(II) with weak bases are explored.

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Chapter 2: Synthesis and Structural Characterization of New Polyether Complexes of Germanium(II)

2.1 Introduction

Our research group has long been interested in the synthesis and characterization of polyether complexes containing group 14 elements in low oxidation state. As previously mentioned, the chemistry involving group 14 cations and polyethers ligands has been an area of great interest over the last decade.[1] The complexation of lead(II) ions by macrocyclic polyethers in solution was well established by the early 1980s,[2] and accordingly, lead(II) and tin(II) were the first group 14 elements to form polyether complexes, which were structurally confirmed by single crystal X-ray diffraction.[3,4] While it was generally thought that low valent germanium centers require stabilization by strongly bound covalent ligands, the isolation of cryptand[2.2.2]-encapsulated germanium(II) dication **A** (**Figure 2.1**) by the Baines group in 2008 caused this paradigm to shift[5] and paved the path for the isolation of many other polyether complexes of germanium(II) in the years that followed.[6–9] Many of the resulting compounds hold great potential for further reactivity in that they may act as Lewis acids to simple nucleophiles like water and ammonia while retaining a non-bonding electron pair.[10]

An overwhelming majority of these cationic crown ether or glyme complexes are paired with triflate counter anions or anions derived from chloride anions, with the heavier halides being present in only a handful of examples.[7,11] As a part of our group's long-standing interest in the synthesis and reactivity of polyether complexes of group 13

and 14 elements,[12,13] we sought to fill this gap by examining in detail the reactions between germanium(II) bromide with various cyclic and acyclic polyethers.

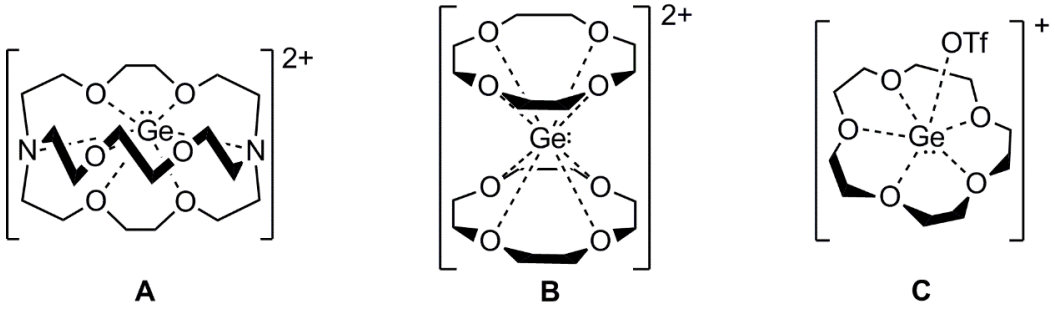


Figure 2.1 Examples of polyether complexes of germanium cations

2.2 Results and Discussions

2.2.1 Germanium(II) Crown Complexes

We began our investigations with the reactions of various crown ethers with commercially available $GeBr_2$. While we obtained crystalline material from several of these reactions, we found that these products were contaminated with significant amounts of ammonium. In several instances, single crystal X-ray diffraction experiments of these materials revealed crown ether ammonium complexes with $GeBr_3^-$ anions (**Figure 2.2** depicts $[NH_4$(benzo[18]crown-6)$][GeBr_3]$ as an example). We discovered that the source of the contamination was the commercially purchased $GeBr_2$: when dissolved in MeCN-d_3 and subjected to a ^{1}H NMR experiment, the spectrum features a 1:1:1 triplet centered at 5.86 ppm, the multiplicity of which is due to coupling of the protons to the ^{14}N isotope (I = 1, 99.63% abundant). Examination of the early literature suggests that this contamination is introduced as part of the purification process for commercially synthesized $GeBr_2$ and would likely go unnoticed for other reactions which do not involve ligands with a high

affinity for ammonium.[14] While the addition of crown ethers almost certainly produced the desired reaction with $GeBr_2$ (due to the presence of $GeBr_3^-$ anions), the crown ethers' large binding affinity for ammonium[15] likely resulted in the displacement of the $GeBr^+$ cation, whose fate remains unknown.

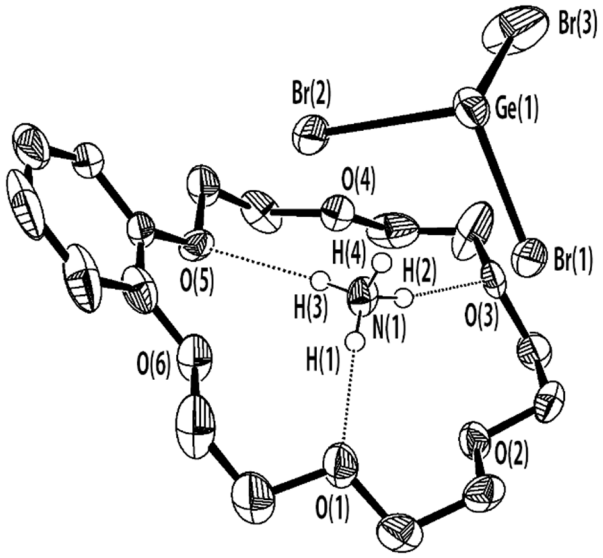
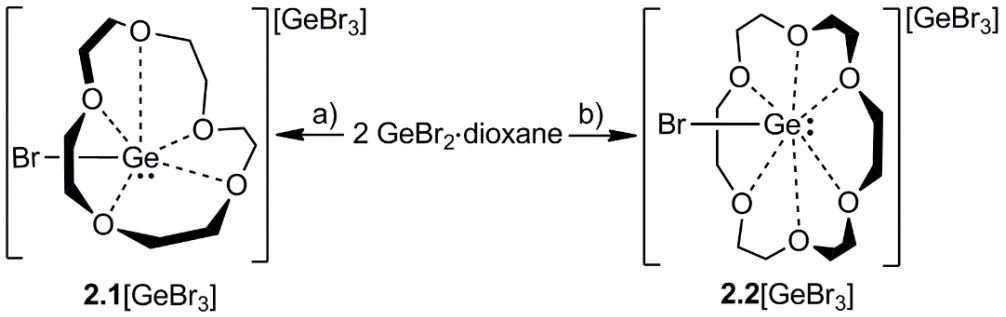


Figure 2.2 Thermal ellipsoid plot (50% probability surface) of **[NH_4(benzo[18]crown-6)][$GeBr_3$]**. Hydrogen atoms (except those of ammonium) are omitted for clarity. Selected bond lengths (Å): H1-O1, 2.10(9), H2-O3, 1.88(12); H3-O5, 2.20(10).

To solve the problem of ammonium contamination, we decided to synthesize $GeBr_2$·dioxane from commercially purchased $GeBr_4$, which is produced using a method that does not involve ammonia.[16] Treatment of two equivalents of $GeBr_2$·dioxane with one equivalent of [15]crown-5 and [18]crown-6 resulted in clean reactions to yield the salts [GeBr([15]crown-5)][$GeBr_3$], **2.1**[$GeBr_3$] and [GeBr([18]crown-6)][$GeBr_3$], **2.2**[$GeBr_3$] respectively (**Scheme 2.1**). Indeed, NMR data as well as elemental analyses of the materials isolated upon workup show no traces of ammonium and indicate that the materials obtained

were analytically pure. The ^{1}H NMR signals for the crown ether protons in each complex (**2.1**[$GeBr_3$] = 3.83 ppm and **2.2**[$GeBr_3$] = 3.81 ppm) are significantly deshielded from those of the free crowns (ca. 3.5 ppm for both free crowns), which confirms formation of the complexes in solution. Recrystallization of the materials to give single crystals suitable for X-ray diffraction was done by adding an appropriate anti-solvent to a dissolved sample, cooling to -30 °C and storing over several days.



Scheme 2.1 Synthesis of **2.1**[$GeBr_3$] and **2.2**[$GeBr_3$]; a) [15]crown-5), b) [18]crown-6

The crystals of **2.1**[$GeBr_3$] are isomorphous to the chloride analogue reported by our group,[6] crystallizing in the orthorhombic space group $Pca2_1$ (**Table 2.1**) with four crystallographically independent units in the asymmetric unit (extended structure provided in Appendix I). The crown ethers of the cations adopt a folded geometry (**Figure 2.3**) wherein the germanium centre retains an apparent stereochemically active lone pair adjacent to the Ge-Br bond. The Ge-O distances in all four crystallographically unique cations range between 2.088(10) and 3.023(9) Å.

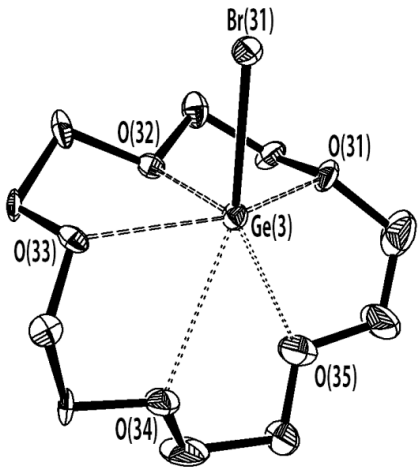


Figure 2.3 Thermal ellipsoid plot (50% probability surface) of **2.1**[$GeBr_3$]. Only one crystallographically unique cation is displayed for clarity. Hydrogen atoms and the anion are omitted for clarity. Dashed lines are used for Ge-O contacts shorter than 2.5 Å and dotted lines are used to indicate Ge-O contacts longer than 2.8 Å. Selected interatomic distances (Å) and angles (°): Ge3-Br31, 2.525(2); Ge3-Ge3-O31, 2.353(9); Ge3-O32, 2.135(9); Ge3-O33, 2.35(3); Ge3-O34, 2.857(10); Ge3-O35, 2.900(10); Br31-Ge3-O31, 89.2(7); Br31-Ge3-O32, 88.5(3); Br31-Ge3-O33, 95.1(2).

As illustrated in **Figure 2.3**, the salt **2.1**[$GeBr_3$] consists of a $GeBr^+$ cation encapsulated by [15]crown-5 rather than a dication as observed in cryptand **(A)** or in the sandwich-like structure of [Ge([12]crown-4)$_2$] $^{+2}$ **(B),** both illustrated in **Figure 2.1**. The shortest Ge-O distance of 2.088(10) Å in all four crystallographically unique cations, is considerably shorter than Ge-O distances observed in **A** and **B** (range from 2.383(6) to 2.489(7) Å and the typical Ge-O single-bond lengths range from 1.75 to 1.85 Å).[5,6]

In the folded conformation of **2.1,** the plane defined by Ge3, O31, O32, and O33 is almost perpendicular to the plane defined by Ge3, O34, and O35. O32 shows the closest contact of 2.135(9) Å; O31 and O33, also show close contacts of 2.353(9) Å and 2.35(3) Å. As a result of folding of the ring, O34 and O35, are situated significantly farther away

at 2.882(10) Å and 2.956(12) Å. The $GeBr^+$ fragment is positioned almost perpendicular on the plane defined by O31, O32, O33 as illustrated **Figure 2.3**.

[GeBr([18]crown-6)][$GeBr_3$], **2.2**[$GeBr_3$] crystallizes in the triclinic space group P-1 (**Table 2.2**) with two unique chemical units in the asymmetric unit (because both are similar, only one is shown in **Figure 2.4**). The two chemical units and the anions $[GeBr_3]^-$ are illustrated in the extended structures provided in the supplementary information (Appendix I). The $GeBr^+$ fragment is bound in a meridional fashion around the Ge(II) ion, but is slightly off-centre in the crown cavity (i.e. the Ge atom is not located at the centroid of the O_6 ring). As such, the Ge-O distances range from 2.269(2) to 3.300(3) Å in the fragment depicted in **Figure 2.4**. The Ge-O distances of the second crystallographically unique cation also fall within this range. This observation illustrates the relatively poor size match between germanium(II) ion and the [18]crown-6 cavity.

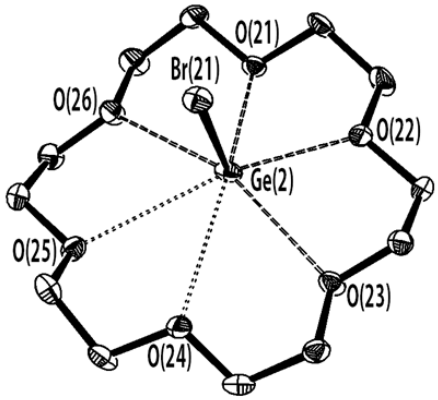
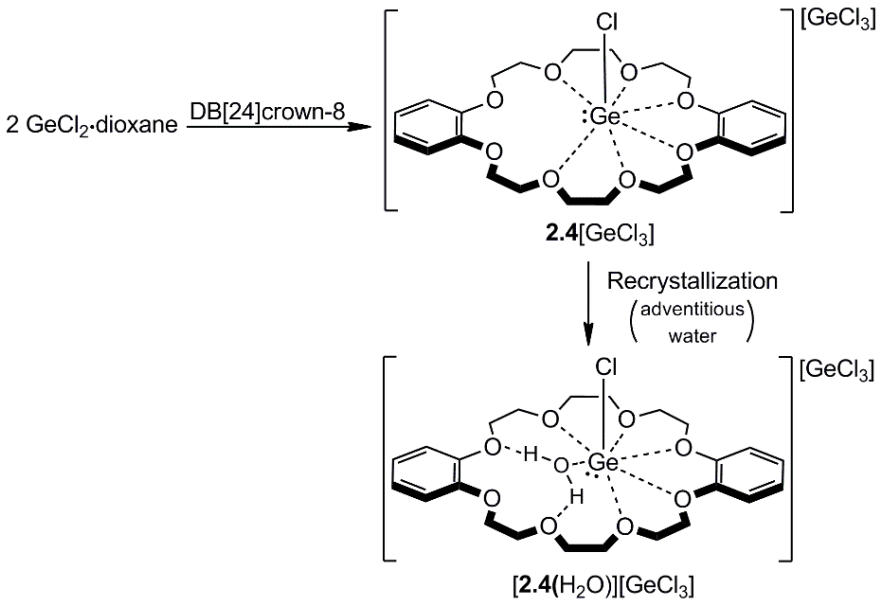


Figure 2.4 Thermal ellipsoid plot (50% probability surface) of **2.2**[$GeBr_3$]. Hydrogen atoms and the anion are omitted for clarity. Dashed lines are used for Ge-O contacts shorter than 3 Å and dotted lines are used to indicate Ge-O contacts longer than 3 Å. Selected interatomic distances (Å) and angles (°): Ge2-Br21, 2.3993(5); Ge2-O21, 2.269(2); Ge2-O22, 2.413(3); Ge2-O23, 2.889(3); Ge2-O24, 3.300(3); Ge2-O25, 3.043(3); Ge2-O26, 2.556(3); Br21-Ge2-O21, 92.61(7); Br21-Ge2-O22, 88.13(7); Br21-Ge2-O23, 96.12(6); Br21-Ge2-O25, 88.70(5); Br21-Ge2-O26, 87.11(6).

The complexation of germanium using larger crown ether ligands (>[18]crown-6) has been nearly completely unexplored. The reaction of dibenzo[24]crown-8 with two equivalents of $GeBr_2$·dioxane in THF followed by subsequent workup did afford a white solid whose NMR spectra and microanalysis was consistent with [GeBr(dibenzo[24]crown-8)][$GeBr_3$], **2.3**[$GeBr_3$], however we were unable to obtain single crystals of this material suitable for X-ray diffraction. The chloride analogue of this compound has also hitherto eluded report, and thus we investigated the analogous reaction involving $GeCl_2$·dioxane as well. Workup of this reaction afforded a white powder whose microanalysis and NMR spectra are consistent with [GeCl(dibenzo[24]crown-8)][$GeCl_3$], **2.4**[$GeCl_3$] (**Scheme 2.2**).



Scheme 2.2 Synthesis of **2.4**[$GeCl_3$] and isolation of [**2.4**(H_2O)][$GeCl_3$]

Recrystallizations of **2.4**[$GeCl_3$] in DCM led to the formation of single crystals of [(H_2O)GeCl(dibenzo[24]crown-8)][$GeCl_3$], [**2.4**(H_2O)][$GeCl_3$], presumably due to adventitious amounts of water in the DCM used for crystallization. The formation of the

water complex [**2.4**(H_2O)][$GeCl_3$] was further confirmed by elemental analysis, multinuclear NMR spectroscopy and FTIR of the isolated crystals. The ^{1}H NMR spectrum of the crystals clearly indicates the presence of the water protons, which appear as a broad peak at 6.41 ppm. In the solid-state structure of [**2.4**(H_2O)][$GeCl_3$], the distances between the Ge atom and the crown ether oxygens ranges from 2.2954(18) to 3.5699(19) Å, while the Ge-OH_2 distance is 2.029(4) Å. The protons of the H_2O molecule are hydrogen bonded to the O-atoms of the crown ether (OH-O lengths are 2.07(7) Å and 1.95(7) Å), placing the water molecule within the confines of the large crown ether (**Figure 2.5**), reminiscent of an example involving indium(III).[17]

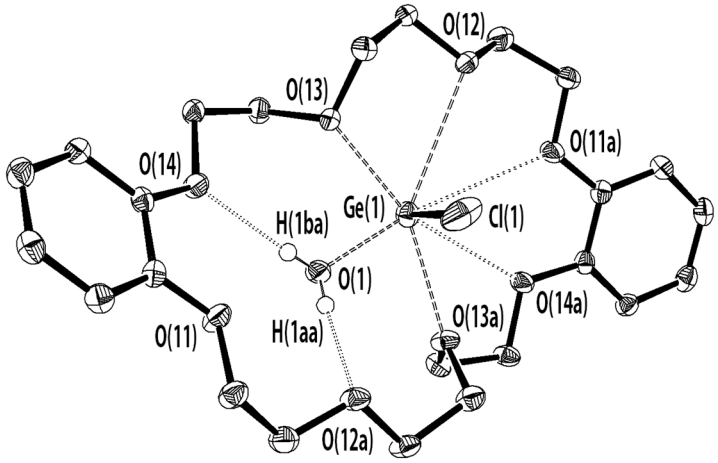


Figure 2.5 Thermal ellipsoid plot (50% probability surface) of [**2.4(**H_2O)][$GeCl_3$]. Hydrogen atoms (except those on H_2O) and the anion are omitted for clarity. Dashed lines are used for Ge-O contacts shorter than 3 Å and dotted lines are used to indicate Ge-O contacts longer than 3 Å. Selected interatomic distances (Å) and angles (°): Ge1-Cl1, 2.2760(12); Ge1-O1, 2.029(4); Ge1-O11a, 3.5699(19); Ge1-O12, 2.9941(18); Ge1-O13, 2.2954(18); Ge1-O14a, 3.3609(19); H1aa-O12a, 1.95(7); H1ba-O14, 2.07(7); Cl1-Ge1-O1, 89.10(13).

Surprisingly, given the considerable reactivity exhibited by most divalent germanium compounds, in 2013 our group reported the first crystallographically

characterized water adduct of germanium(II),[10] making this a rare example of such a compound. In a related note, only a handful of structurally authenticated germanium(IV) water complexes have been reported, but such species all have much shorter Ge-O distances of less than 2 Å as one might expect.[18–20] The unexpected isolation of a new water complex of germanium(II) featuring such a different bonding motif is remarkable given the foregoing.

FTIR studies further confirmed the formation of this remarkable water complex. The FTIR spectrum of [**2.4**(H_2O)][$GeCl_3$], illustrated in **Figure 2.6**, contains a peak at 3242 cm^{-1} which clearly indicates the presence of H-bonded O-H stretch.

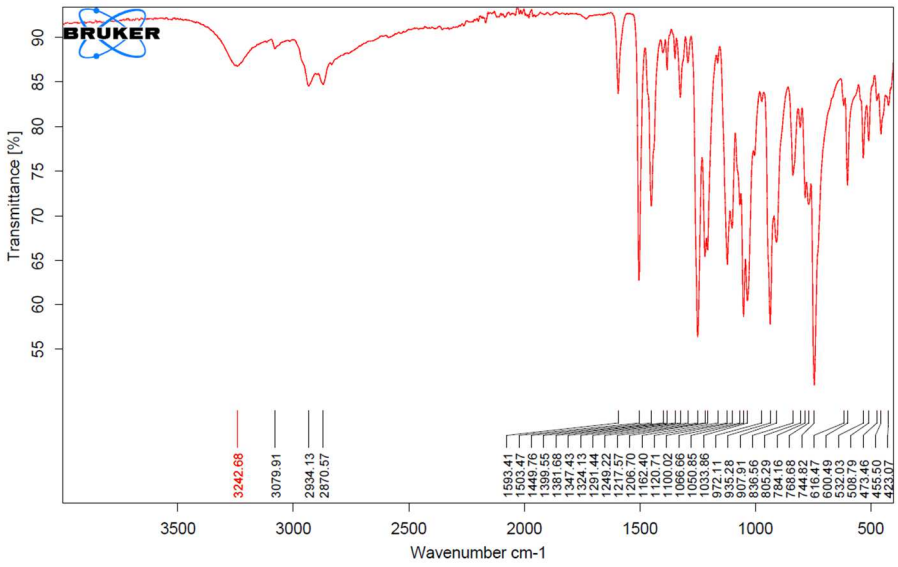
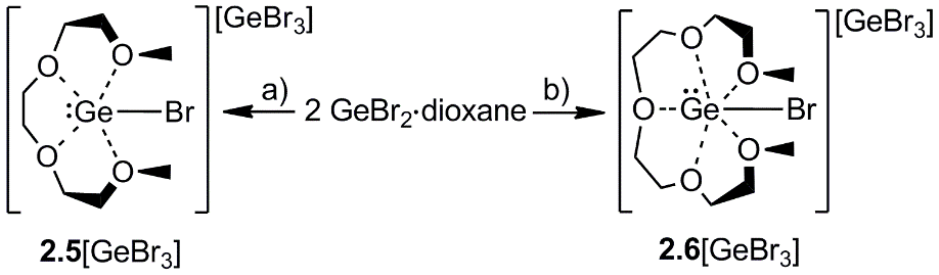


Figure 2.6 FTIR spectrum of [(H_2O)GeCl(dibenzo[24]crown-8)][$GeCl_3$]

Crystallographic data for the complexes synthesized and structurally characterized, including [NH_4(benzo[18]crown-6)][$GeBr_3$] complex and the water adduct [(H_2O)GeCl(dibenzo[24]crown-8)][$GeCl_3$] are summarized in **Table 2.1** and **Table 2.2**.

2.2.2 Germanium(II) Bromide Glyme Complexes

We next sought to investigate the reaction of $GeBr_2$ with glymes. The much higher degree of flexibility in glymes should theoretically give rise to different structural motifs than those observed in the crown ether analogues. Furthermore, to our knowledge there are no structurally authenticated germanium glyme complexes yet reported. The treatment of two equivalents of $GeBr_2$·dioxane with triglyme or tetraglyme followed by workup led to the isolation of [GeBr(triglyme)][$GeBr_3$], **2.5**[$GeBr_3$] and [GeBr(tetraglyme)][$GeBr_3$], **2.6**[$GeBr_3$] respectively as analytically pure white solids **(Scheme 2.3**). As with the crown ether complexes, the ^{1}H NMR spectra of these materials feature signals that are slightly deshielded compared to those of their respective free glymes, indicative of complexation in solution.



Scheme 2.3 Synthesis of **2.5**[$GeBr_3$] and **2.6**[$GeBr_3$]; a) triglyme, b) tetraglyme

2.5[$GeBr_3$] was recrystallized to form crystals suitable for SC-XRD by addition of hexanes to a concentrated toluene solution and storage at -30°C. The salt crystallizes in the triclinic space group P-1 (**Table 2.3**) with a single cation and anion in the asymmetric unit. The triglyme binds the germanium(II) atom in a *mer*-fashion, as one would expect for the more flexible glyme, with Ge-O distances ranging from 2.122(3) to 2.656(4) Å, two being short distances, one intermediate and a longer distance. Germanium is situated closer to

O12 and O13 at distances of 2.122(3) Å and 2.189(3) Å and the two terminal oxygen atoms, O11 and O14, are situated further at 2.425(4) Å and 2.656(4) Å (**Figure 2.7**). The Ge-O distances are compared to the range for typical Ge-O single bonds at 1.75-1.85 Å.[6] Although these distances are longer than the typical Ge-O bond lengths, all are comparable to Ge-O_{crown} distances for the Ge(II) crown ether complexes and the related complexes, reported by our group and other research groups.[5–7] The Ge–Br bond length of the cation is 2.4155(9) Å, which is consistent with reported Ge-Br bond lengths[21,22] and with the average 2.4(1) Å calculated for germanium compounds with this type of Ge-Br contact.[23] Ge-Br bond lengths in the anion $[GeBr_3]^-$ (extended structure illustrated in Appendix I) range from 2.4549(9) to 2.506(3) Å which is in the same range with the reported values.[23]

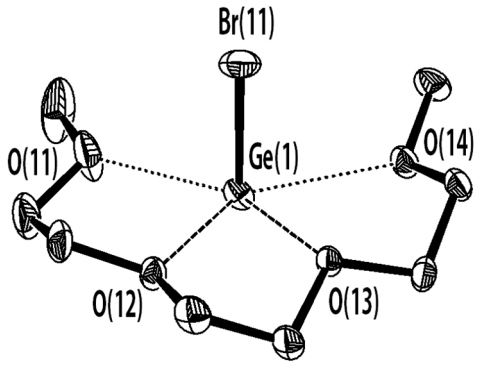


Figure 2.7 Thermal ellipsoid plot (50% probability surface) of **2.5**[$GeBr_3$]. Hydrogen atoms and the anion are omitted for clarity. Dashed lines are used for Ge-O contacts shorter than 2.2 Å and dotted lines are used to indicate Ge-O contacts longer than 2.4 Å. Selected interatomic distances (Å) and angles (°): Ge1-Br11, 2.4155(9); Ge1-O11, 2.425(4); Ge1-O12, 2.122(3); Ge1-O13, 2.189(3); Ge1-O14, 2.656(4); Br11-Ge1-O11, 85.09(15); Br11-Ge1-O12, 94.65(11); Br11-Ge1-O13, 87.10(11); Br11-Ge1-O14, 87.96(10).

As mentioned above, the ^1H and ^{13}C NMR chemical shifts also confirm complexation by tryglyme in solution, the signals being considerably deshielded compared

to those of the free glyme. The ^{1}H NMR resonances range from 3.4 to 3.8 ppm and the ^{13}C NMR chemical shifts range from 58 to 72 ppm.

Crystals of **2.6**[$GeBr_3$] suitable for single crystal X-ray diffraction were obtained by diffusion of pentane into a saturated THF solution. The salt crystallizes in the monoclinic space group $P2_1/c$ (**Table 2.3**) with one ion pair in the asymmetric unit. As with the triglyme case, the tetraglyme binds the germanium(II) atom in a *mer*-fashion. The Ge-O distances range between 2.219(3) and 2.805(4) Å, with the more terminal oxygen atoms O11 at the distance of 2.710(3) Å, and respectively, O15 at 2.805(4) Å having the larger Ge-O distance. The closest to Ge centre is O13, at a distance of 2.219(3) Å, followed by O12 and O14 at two close distances of 2.389(3) and 2.364(3) Å, respectively (**Figure 2.8**). As with the triglyme complex, the Ge–Br bond length of the cation is 2.4003(3) Å, which is almost identical to the calculated average of 2.4(1) Å reported.[23]

The signals in ^{1}H and ^{13}C NMR spectra are also deshielded, as in the case of the triglyme complex, confirming complexation by tetraglyme in solution. The ^{1}H NMR resonances range from 3.4 to ca. 3.9 ppm and the ^{13}C NMR chemical shifts range from 58 to 71 ppm.

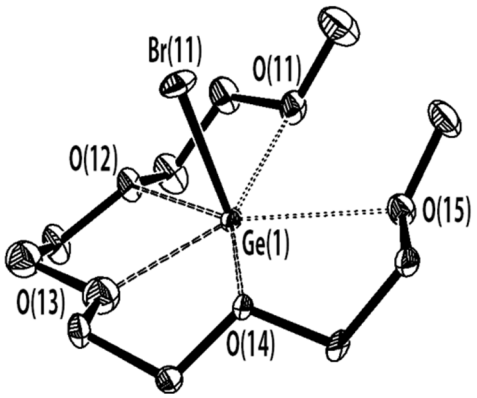


Figure 2.8 Thermal ellipsoid plot (50% probability surface) of **2.6**[$GeBr_3$]. Hydrogen atoms and the anion are omitted for clarity. Dashed lines are used for Ge-O contacts shorter than 2.4 Å and dotted lines are used to indicate Ge-O contacts longer than 2.7 Å. Selected interatomic distances (Å) and angles (°): Ge1-Br11, 2.4003(7); Ge1-O11, 2.710(3); Ge1-O12, 2.389(3); Ge1-O13, 2.219(3); Ge1-O14, 2.364(3); Ge1-O15, 2.805(4); Br11-Ge1-O11, 90.80(9); Br11-Ge1-O12, 89.68(7); Br11-Ge1-O13, 92.79(11); Br11-Ge1-O14, 88.65(10); Br11-Ge1-O15, 88.49(8).

By analysing the data obtained for these glyme complexes, we can conclude that the structures of **2.5** and **2.6** feature very similar characteristics. Both, triglyme and tetraglyme adopt planar conformations, binding the germanium(II) atom in a belt-like manner, with symmetric Ge-O distances. The Ge_{cation}-Br_{anion} distances range from 3.4957(7) to 7.2177(8) Å for both glyme complexes. The shortest distance of 3.4957(7) Å lies well outside of the range for typical Ge-Br bond lengths,[23] clearly indicating a separated $GeBr_3^-$ anion.

2.3 Conclusions

The reactions between commercially available germanium(II) bromide and various crown ethers results in the formation of ammonium-crown ether $GeBr_3^-$ salts due to the presence of ammonium in commercially available germanium(II) bromide. The use of

in-house synthesized $GeBr_2$·dioxane solves the issue of ammonium contamination, and using this precursor, the salts [GeBr([15]crown-5)][$GeBr_3$], [GeBr([18]crown-6)][$GeBr_3$], [GeBr(triglyme)][$GeBr_3$] and [GeBr(tetraglyme)][$GeBr_3$] were isolated and their crystal structures determined. The latter two complexes are the first examples of crystallographically confirmed glyme complexes of germanium. The synthesis of [GeBr(dibenzo[24]crown-8)][$GeBr_3$] and [GeCl(dibenzo[24]crown-8)][$GeCl_3$] are also reported. The water adduct of the latter salt, [(H_2O)GeCl(dibenzo[24]crown-8)][$GeCl_3$] was characterized by X-ray crystallography and the larger crown ether accommodates the $[GeCl]^+$ fragment and a water molecule within its cavity and represents a rare example of a germanium(II) water adduct. All the complexes were structurally characterized and confirmed by elemental analysis and multinuclear NMR spectroscopy. The water complex was further confirmed by FTIR, the spectrum clearly showing the O-H stretch at 3242 cm^{-1}.

2.4 Experimental

2.4.1 General procedures

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma Aldrich. MeCN-d_3 was dried over calcium hydride or phosphorus pentoxide and stored over molecular sieves under nitrogen. All other solvents were dried on a series of Grubbs' type columns and were degassed prior to use.[24] Glymes were dried over 3Å molecular sieves and degassed prior to use. $GeBr_2$·dioxane was synthesized by modification of a literature procedure for the synthesis of $GeCl_2$·dioxane.[16] NMR spectra were recorded at room temperature on Bruker Avance III 500 MHz, Bruker Avance Ultrashield 300 MHz or Bruker Avance DPX 300 MHz

spectrometers. Chemical shifts (δ) are reported in ppm relative to internal standards for ^{1}H and ^{13}C (for the given deuterated solvent). Elemental analysis was performed at the University of Windsor Mass Spectrometry Service Laboratory using a Perkin Elmer 2400 combustion CHN analyzer. IR spectra were obtained using a Bruker Alpha FT-IR spectrometer equipped with a Platinum single reflection diamond ATR module; stretching frequencies are reported in cm^{-1}. Melting points were determined under a N_2 atmosphere. Electrospray ionization mass spectrometry was attempted at the McMaster Regional Centre for Mass Spectrometry but none of the species herein withstand the ionization process, and only alkali metal-crown complexes are typically observed in the spectra.

2.4.2 Specific Procedures

Synthesis of [GeBr([15]crown-5)][$GeBr_3$], 2.1[$GeBr_3$]

[15]crown-5 (0.154 mL, 0.757 mmol) was added to a $GeBr_2$·dioxane (0.500 g, 1.56 mmol) solution in THF (ca. 40 mL). The colourless solution stirred for 2 hours at room temperature. All volatile components were then removed under reduced pressure. The resultant oily product was washed with hexanes (5 mL x 3) to provide a white solid. Crystals suitable for SC-XRD were obtained by diffusion of pentane into a saturated THF solution at −30 °C. **Yield:** 86% (0.463 g, 0.675 mmol). **Mp:** 121–123 °C. **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.83 (s). **$^{13}C\{^{1}H\}$ NMR (CD_3CN, 300 MHz) δ:** 70.1 (s). **Anal. Calcd** for $C_{10}H_{20}Br_4Ge_2O_5$·0.25 THF: C, 18.79; H, 3.15. Found: C, 18.91; H, 3.14 (**Anal. Calcd** for $C_{10}H_{20}Br_4Ge_2O_5$: C, 17.53; H, 2.94). The presence of a small amount of residual THF was confirmed by ^{1}H NMR.

Synthesis of [GeBr([18]crown-6)][$GeBr_3$], 2.2[$GeBr_3$]

A solution of [18]crown-6 (0.080 g, 0.303 mmol) in acetonitrile (ca. 1 mL) was added to a solution of $GeBr_2$·dioxane (0.200 g, 0.624 mmol) in acetonitrile (ca. 40 mL). After stirring overnight at room temperature all volatile components were removed under reduced pressure. The resultant white solid was washed with hexanes (4 mL x 2) and dried in vacuo. Colourless crystals of **2.2**[$GeBr_3$] suitable for SC-XRD were obtained by slow diffusion of Et_2O into a saturated acetonitrile solution at −30 °C. **Yield:** 88% (0.202 g, 0.277 mmol). **Mp:** 94–98 °C. **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.81 (s). **$^{13}C\{^1H\}$ NMR (CD_3CN, 300 MHz) δ:** 70.7 (s). **Anal. Calcd** for $C_{12}H_{24}Br_4Ge_2O_6$: C, 19.76; H, 3.32. Found: C, 20.16; H, 3.15.

Synthesis of [GeBr(Dibenzo[24]crown-8)][$GeBr_3$], 2.3[$GeBr_3$]

A solution of dibenzo[24]crown-8 (0.140 g, 0.312 mmol) in THF (ca. 1 mL) was added to a solution of $GeBr_2$·dioxane (0.200 g, 0.624 mmol) in THF (ca. 40 mL). The colourless solution was stirred for 2 hours at room temperature. All volatile components were removed under reduced pressure. The resultant white solid was washed with hexanes (4 mL x 2), yielding a solid powder. **Yield:** 64% (0.184 g, 0.201 mmol). **Mp:** 92–94 °C. **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.70 (s, 8H), 3.82 (m, 8H), 4.15 (m, 8H), 6.97 (m, 8H). **$^{13}C\{^1H\}$ NMR (CD_3CN, 300 MHz) δ:** 69.54 (s), 69.80 (s), 70.43 (s), 115.43 (s), 122.95 (s), 149.54 (s**). Anal. Calcd** for $C_{24}H_{32}O_8Ge_2Br_4$: C, 31.55; H, 3.53. Found: C, 31.56; H, 3.37.

Synthesis of [GeCl(dibenzo[24]crown-8)][$GeCl_3$], 2.4[$GeCl_3$] and isolation of [2.4(H_2O)][$GeCl_3$]

A solution of dibenzo[24]crown-8 (0.290 g, 0.646 mmol) in THF (ca. 1 mL) was added to a solution of $GeCl_2$·dioxane (0.300 g, 1.29 mmol) in THF (ca. 40 mL). The colourless solution was stirred for 2 hours at room temperature. All volatile components were removed under reduced pressure. The resultant white solid was washed with hexanes (4 mL x 2) and allowed to dry, yielding the analytically pure title compound. **Yield:** 93% (0.432 g, 0.587 mmol). **Mp:** 103–105°C. **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.70 (s, 8H), 3.81 (m, 8H), 4.11 (m, 8H), 6.92 (m, 8H). **$^{13}C\{^1H\}$ NMR (CD_3CN, 300 MHz) δ:** 69.43 (s), 70.45 (s), 71.28 (s), 114.91 (s), 122.39 (s), 149.56 (s). **Anal. Calcd** for $C_{24}H_{32}Cl_4Ge_2O_8$: C, 39.18; H, 4.38. Found: C, 39.78; H, 4.45.

Recrystallization of this material by slow evaporation of DCM yielded a single crystal of [**2.4**(H_2O)][$GeCl_3$] suitable for SC-XRD, presumably due to adventitious water in the DCM.

[2.4(H_2O)][$GeCl_3$]

Mp: 105-108°C. **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.78 (s, 8H), 3.89 (m, 8H), 4.11 (m, 8H), 6.41 (s, 2H, H_2O), 6.94 (m, 8H). **$^{13}C\{^1H\}$ NMR (CD_3CN, 300 MHz) δ:** 69.64(s), 70.45 (s), 71.35 (s), 115.14 (s), 122.46 (s), 149.71(s). **Anal. Calcd** for $C_{24}H_{34}Cl_4Ge_2O_9$: C, 38.25; H, 4.55. Found: C, 38.94; H, 4.29. **FTIR**: O–H = 3242 cm^{-1}

Synthesis of [GeBr(triglyme)][$GeBr_3$], 2.5[$GeBr_3$]

A solution of triglyme (0.141 mL, 0.780 mmol) in THF (ca. 1 mL) was added dropwise to a solution of $GeBr_2$·dioxane (0.500 g, 1.56 mmol) in THF (40 mL). The resultant colourless solution was stirred for 2 hours at room temperature followed by removal of all volatile components under reduced pressure to afford a colourless oil. The oily residue was washed in hexanes (5 mL x 3) and decanted yielding a solid product. Small crystals suitable for SC-XRD were obtained by adding hexanes to a concentrated toluene solution and storing at -30°C. **Yield:** 71 % (0.357 g, 0.555 mmol). **Mp:** 45–47 °C. **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.41 (s, 6H), 3.60 (m, 4H), 3.79 (m, 8H).**^{13}C{^{1}H} NMR (CD_3CN, 300 MHz) δ:** 58.97 (s), 70.77 (s), 70.82 (s), 72.3 (s**). Anal. Calcd** for $C_8H_{18}Br_4Ge_2O_4$: C, 14.94; H, 2.82. Found: C, 15.43; H, 2.52.

Synthesis of [GeBr(tetraglyme)][$GeBr_3$], 2.6[$GeBr_3$]

A solution of tetraglyme (0.171 mL, 0.779 mmol) in THF (ca. 1 mL) was added dropwise to a solution of $GeBr_2$·dioxane (0.500 g, 1.56 mmol) in THF (40 mL). The resultant colourless solution was stirred for 2 hours at room temperature followed by removal of all volatile components under reduced pressure to afford a colourless oil. The oily residue was washed in hexanes (5 mL x 3) to give a white solid. Crystals suitable for SC-XRD were obtained by diffusion of pentane into a saturated THF solution at −30 °C. **Yield:** 79% (0.422 g, 0.614 mmol). **Mp:** 57–60 °C. **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.41 (s, 6H), 3.65 (m, 4H), 3.81 (m, 8H), 3.88 (m, 4H). **^{13}C{^{1}H} NMR (CD_3CN, 300 MHz) δ:** 58.88 (s), 70.11 (s), 70.68 (s), 70.72 (s), 71.6 (s). **Anal. Calcd** for $C_{10}H_{22}Br_4Ge_2O_5$: C, 17.48; H, 3.23. Found: C, 18.09; H, 3.43.

2.4.3 X-ray crystallography

Crystals for investigation were covered in Paratone®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N_2 of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXIII software suite[25] on a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with MoK_α ($\lambda = 0.71073$ Å) or CuK_α ($\lambda = 1.54178$ Å) radiation. For each sample, data were collected at low temperature. APEXIII software was used for data reductions and SADABS[26] was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX[27] software suite as implemented in the WinGX[28] or OLEX2[29] program suites. Validation of the structures was conducted using PLATON[30] and the structures have been deposited in the Cambridge Structural Database (CCDC 1813785-1813794). As with many complexes of this type, several of the compounds exhibited disorder within the polyether groups; this was treated with variable occupancy 2-site models in which appropriate restraints were used to restrain the thermal parameters of related atoms to be approximately equal.

Table 2.1 Summary of crystallographic data and refinement details for **[NH_4(benzo[18]crown-6)][$GeBr_3$]** and **2.1[$GeBr_3$]**

Compound	**[NH_4(benzo[18]crown-6)][$GeBr_3$]**	**2.1[$GeBr_3$]**
CCDC	1813785	1813786
Empirical formula	$C_{16}H_{28}Br_3GeNO_6$	$C_{10}H_{20}Br_4Ge_2O_5$
Formula weight	642.71	685.08
Color, habit	Colorless, irregular	Colorless, prism
Crystal size/mm^3	0.276 × 0.27 × 0.125	0.17 × 0.16 × 0.04
Temperature/K	170.01	173(2)
Crystal system	Triclinic	Orthorhombic
Space group (ASP)	P-1	$Pca2_1$
a/Å	9.9071(6)	30.7572(8)
b/Å	10.4679(6)	10.1827(3)
c/Å	12.8109(7)	24.6466(7)
α/°	75.657(3)	90
β/°	71.941(3)	90
γ/°	70.339(3)	90
Volume/$Å^3$	1174.12(12)	7719.1(4)
Z	2	16
$\rho_{calc}g/cm^3$	1.818	2.358
μ/mm^{-1}	6.438	13.683
F(000)	632.0	5184
Radiation	MoKα	CuKα
Reflections collected	27805	168614
Independent reflections	4460	11070
R_{int}	0.132	0.101
Data/restraints/parameters	4460/0/269	11070/122/750
Goodness-of-fit on F2	1.023	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.046 wR_2 = 0.080	R_1 = 0.043 wR_2 = 0.061
Final R indexes [all data]	R_1 = 0.106 wR_2 = 0.100	R_1 = 0.057 wR_2 = 0.064
Residual density / e $Å^{-3}$	1.75/-1.80	0.777/-0.734
Data completeness / %	99.4	99.2
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F2	
R1(F): {Σ(|F_o| - |Fc|)/Σ|F_o|} for reflections with F_o > 4(Σ(F_o)). wR2(F2): {Σw(|F_o|2 - |Fc|2)2/Σw(|F_o|2)2}1/2 where w is the weight given to each reflection		

Table 2.2 Summary of crystallographic data and refinement details for **2.2[$GeBr_3$]** and **[2.4(H_2O)][$GeCl_3$]**

Compound	**2.2[$GeBr_3$]**	**[2.4(H_2O)][$GeCl_3$]**
CCDC	1813787	1813788
Empirical formula	$C_{12}H_{24}Br_4Ge_2O_6$	$C_{24}H_{34}Cl_4Ge_2O_9$
Formula weight	729.13	753.49
Color, habit	Colorless, prism	Colorless, irregular
Crystal size/mm^3	0.342 × 0.14 × 0.08	0.19 × 0.15 × 0.078
Temperature/K	130.01	170.01
Crystal system	Triclinic	Monoclinic
Space group (ASP)	P-1	C2/c
a/Å	12.4881(6)	18.2752(6)
b/Å	14.2168(7)	14.8602(5)
c/Å	14.5248(7)	12.0984(5)
α/°	114.3775(18)	90
β/°	90.5269(19)	112.7480(10)
γ/°	107.2282(18)	90
Volume/$Å^3$	2217.70(19)	3030.03(19)
Z	4	4
$\rho_{calc}g/cm^3$	2.184	1.652
μ/mm^{-1}	9.940	2.384
F(000)	1392.0	1528.0
Radiation	MoKα	MoKα
Reflections collected	102138	66191
Independent reflections	12505	3364
R_{int}	0.068	0.055
Data/restraints/parameters	12505/0/433	3364/2/203
Goodness-of-fit on F2	1.067	1.132
Final R indexes [I>=2σ (I)]	R_1 = 0.040 wR_2 = 0.063	R_1 = 0.040 wR_2 = 0.096
Final R indexes [all data]	R_1 = 0.063 wR_2 = 0.069	R_1 = 0.050 wR_2 = 0.101
Residual density / e $Å^{-3}$	1.35/-1.66	1.66/-0.79
Data completeness / %	99.6	99.7
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F2	
R1(F): {Σ(|F_o| - |Fc|)/Σ|F_o|} for reflections with F_o > 4(Σ(F_o)). wR2(F2): {Σw(|F_o|2 - |Fc|2)2/Σw(|F_o|2)2}1/2 where w is the weight given to each reflection		

Table 2.3 Summary of crystallographic data and refinement details for **2.5[$GeBr_3$]** and **2.6[$GeBr_3$]**

Compound	**2.5[$GeBr_3$]**	**2.6[$GeBr_3$]**
CCDC	1813789	1813790
Empirical formula	$C_8H_{18}Br_4Ge_2O_4$	$C_{10}H_{22}Br_4Ge_2O_5$
Formula weight	643.04	687.09
Color, habit	Colorless, plate	Colorless, irregular
Crystal size/mm^3	0.38 × 0.13 × 0.042	0.276 × 0.270 × 0.125
Temperature/K	159.58	135(2)
Crystal system	Triclinic	Monoclinic
Space group (ASP)	P-1	$P2_1/c$
a/Å	6.4660(6)	12.5980(7)
b/Å	10.5524(10)	13.2256(7)
c/Å	13.8420(13)	12.9975(7)
α/°	74.883(4)	90
β/°	88.247(4)	109.434(2)
γ/°	82.493(4)	90
Volume/$Å^3$	903.96(15)	2042.21(19)
Z	2	4
$\rho_{calc}g/cm^3$	2.362	2.235
μ/mm^{-1}	12.167	10.783
F(000)	604.0	1304.0
Radiation	MoKα	MoKα
Reflections collected	26357	165609
Independent reflections	5519	5172
R_{int}	0.067	0.063
Data/restraints/parameters	5519/0/175	5172/0/192
Goodness-of-fit on F2	1.044	1.268
Final R indexes [I>=2σ (I)]	R_1 = 0.051 wR_2 = 0.101	R_1 = 0.038 wR_2 = 0.079
Final R indexes [all data]	R_1 = 0.086 wR_2 = 0.114	R_1 = 0.046 wR_2 = 0.085
Residual density / e $Å^{-3}$	1.51/-1.71	0.85/-1.11
Data completeness / %	99.2	99.9
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F2	
R1(F): $\{\Sigma(\|F_o\| - \|Fc\|)/\Sigma\|F_o\|\}$ for reflections with $F_o > 4(\Sigma(F_o))$. wR2(F2): $\{\Sigma w(\|F_o\|2 - \|Fc\|2)2/\Sigma w(\|F_o\|2)2\}1/2$ where w is the weight given to each reflection		

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Chapter 3: Synthesis and Structural Characterization of New Polyether Complexes of Tin(II)

3.1 Introduction

In recent years, there has been substantial interest in stabilizing group 13 and 14 elements in low oxidation states using crown ethers and their related ligands. More specifically, polyether complexes of indium(I) and germanium(II) have been reported by earlier members of our group[1–3], examples of these complexes are depicted in **Figure 3.1.** In light of this successful work and as a part of our group's long-standing interest in these complexes, we continued to explore the synthesis and reactivities of new complexes of tin(II) halides and tin(II) triflates with crown ethers and glyme ligands.

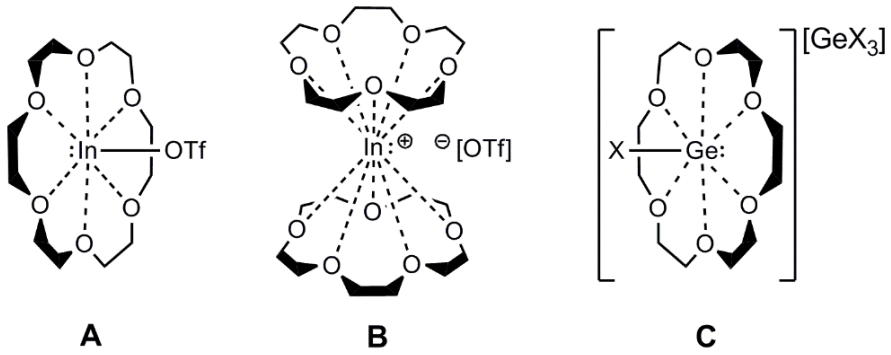


Figure 3.1 Examples of In(I) and Ge(II) crown ethers complexes (OTf=O_3SCF_3; X=Cl, Br)

As seen with the In(I) complexes with [15]crown-5 and [18]crown-6 and the Ge(II) complexes with the same common crown ethers, there are similarities and differences between the structures of these complexes and the Sn(II) analogous complexes;[3] these are based on the size of the crown ethers or the glymes and also on the substituents on the cation (In^+ or Ge^{2+}). While both cations of In(I) and Ge(II) can fit into the cavity of

[18]crown-6 (**Figure 3.1)**, In^{+} forms a sandwich with [15]crown-5, similar to how Ge^{2+} adopts a sandwich structure with the smaller [12]crown-4.[2] A similar chemistry was anticipated for Sn^{2+} given that Sn(II) is isoelectronic with In(I) and isovalent with Ge(II). Examples of various structures of the Sn(II) analogous complexes reported by research groups including ours[3,4] are summarized and illustrated in **Figure 3.2** below.

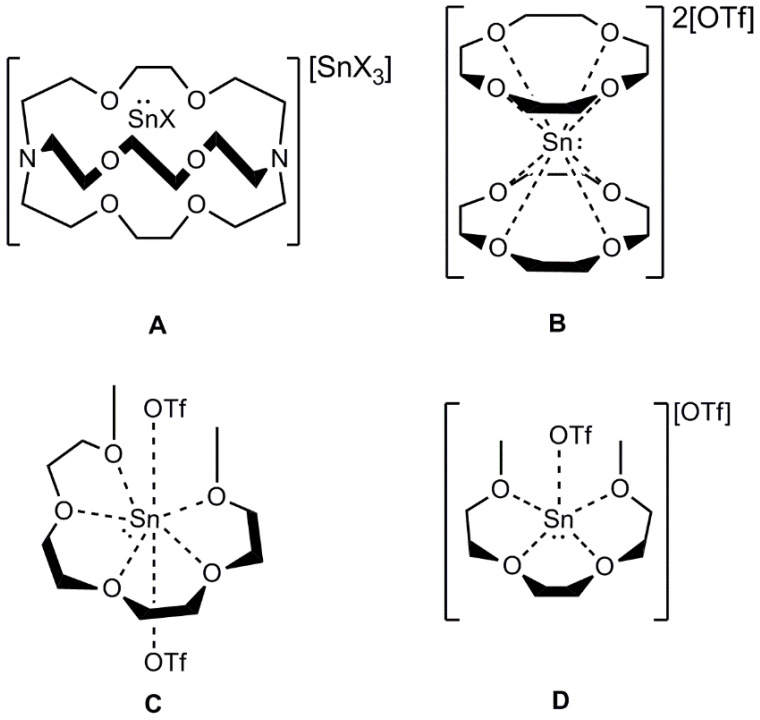


Figure 3.2 Examples of Sn(II) polyether complexes (X=Cl, Br, I)

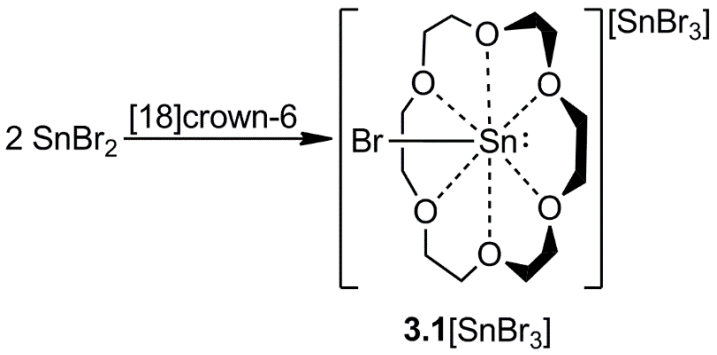
As an extension to previously reported work by our group and research carried out in collaboration with other groups we examined in detail the reactions between tin(II) bromide with various cyclic and acyclic polyethers. Also, we investigated the reaction between tin(II) triflate (triflate = OTf = O_3SCF_3) and a larger size crown ether, such as dibenzo[24]crown-8, with remarkable results. All the results obtained from these various reactions are discussed in the next two sections of this chapter.

3.2 Results and Discussions

3.2.1 Tin (II) Bromide Crown Complexes

Our experience with the ammonium contamination of commercially available $GeBr_2$ prompted us to examine whether the same contamination would be present in commercially purchased $SnBr_2$. We were unable to detect any ammonium contamination by NMR spectroscopy of the commercially purchased $SnBr_2$ and we did not encounter problems with ammonium contamination during our subsequent reactions.

The treatment of two equivalents of $SnBr_2$ with [18]crown-6 afforded the complex [SnBr([18]crown-6)][$SnBr_3$], **3.1**[$SnBr_3$] (**Scheme 3.1**). The product was confirmed to be the salt **3.1**[$SnBr_3$] by single crystal X-ray diffraction, elemental analysis and multinuclear NMR spectroscopy. As with the germanium analogues, the crown ether proton signal in the ^{1}H NMR spectrum at 3.78 ppm is deshielded with respect to the free crown signal (3.51 ppm) which confirms formation of the complex in solution.



Scheme 3.1 Synthesis of **3.1**[$SnBr_3$]

Upon workup, the single crystals suitable for X-Ray diffraction were obtained by slow evaporation of a THF solution. **3.1**[$SnBr_3$] crystallizes in the triclinic space group P-1

(**Table 3.1**), the same space group as the chloride and triflate analogues, [SnCl([18]crown-6)][$SnCl_3$][5] and [Sn([18]crown-6)OTf][OTf].[6] There are four crystallographically independent units in the asymmetric unit of **3.1**[$SnBr_3$]. All four chemical units and anions $[SnBr_3]^-$ are depicted in the extended structure illustrated in the supplementary information (appendix II).

The [18]crown-6 complexes the $SnBr^+$ fragment in a *mer*-fashion and the Sn-O distances range from 2.703(5) to 2.855(6) Å (**Figure 3.3**). The covalent radii of Sn and O are 1.40 Å and 0.73 Å, respectively, and the ionic radii is 0.93 Å for Sn(+2) and 1.40 Å for O(-2), thus the Sn-O distances in **3.1** are much longer than a typical Sn-O bond length but consistent with those in the related tin(II) complexes.[6] Examination of the three structures suggests that complex **3.1** appears to be similar to both analogues [18]crown-6 complexes with $Sn(OTf)_2$ and $SnCl_2$ but is clearly more related to the chloride complex of the form [SnCl([18]crown-6)][$SnCl_3$], reported by Nicholson in 1986.[5] In these two related structures the substituent (Cl or Br) bonded to the tin atom lies nearly normal to the crown ether. The face opposite the substituent does not appear to have any unusually-close contacts and suggests the presence of a stereochemically-active lone pair of electrons.[5,6] The structures can be best described as hexagonal pyramids (or a hexagonal bipyramid if the lone pair is included at the remaining axial position), with the base consisting of the tin and the six oxygen atoms in an approximate plane. It appears that the tin atom is situated slightly below the six oxygen atoms plane on the opposite side to the axial Br atom (**Figure 3.3**).

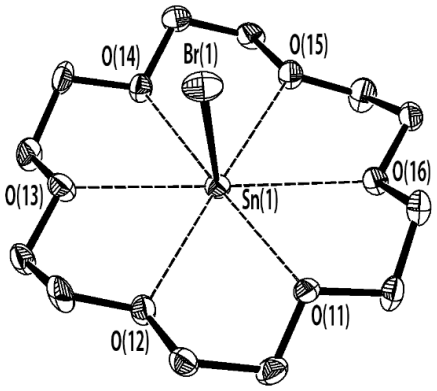
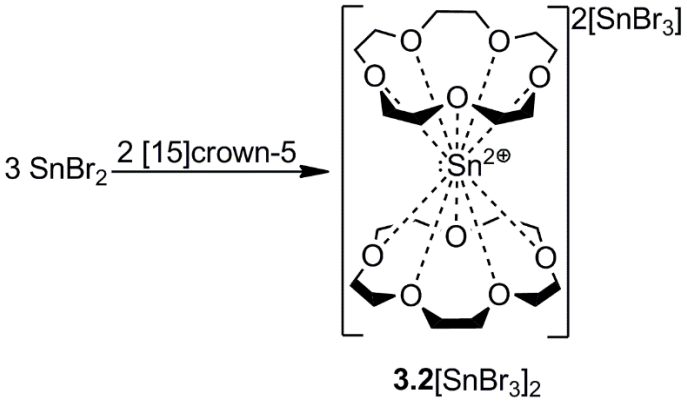


Figure 3.3 Thermal ellipsoid plot (50% probability surface) of **3.1**[$SnBr_3$]. Hydrogen atoms and the anion are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn1-Br1, 2.5979(11); Sn1-O11, 2.855(6); Sn1-O12, 2.745(6); Sn1-O13, 2.703(5); Sn1-O14, 2.764(6); Sn1-O15, 2.733(6); Sn1-O16, 2.740(6); Br1-Sn1-O11, 87.17(11) Br1-Sn1-O12, 93.16(13); Br1-Sn1-O13, 82.81(10); Br1-Sn1-O14, 89.27(12); Br1-Sn1-O15, 87.16(13) Br1-Sn1-O16, 92.68(11).

While the $GeBr^+$ fragment was bound in the same meridional fashion but slightly off-centre in the [18]crown-6 cavity, the tin(II) ion illustrates a better size match with the cavity of the crown, expected for the larger tin. The examination of the structure indicates that the $SnBr^+$ fragment is positioned almost perpendicular to the plane defined by the six oxygen atoms of the crown ring (**Figure 3.3**), as seen in most of the structures of Ge(II) bromide complexes characterised in the previous chapter. The distance Sn1-Br1 of 2.5979(11) Å and all three Sn-Br distances of 2.6679(12), 2.6432(14) and 2.6308(12) Å in the counter anion $[SnBr_3]^-$ are consistent with those in the related tin(II) polyether complexes. The shortest Sn_{cation}-Br_{anion} distance is 3.501(11) Å and lies well outside of the range for typical Sn-Br bond lengths clearly indicating a separated $[SnBr_3]^-$ anion.[4,7] Examination of the structure of complex **3.1** reveals that the 18[crown]-6 bounds the tin atom in a belt-like manner, reminiscent of s-block metal crown ether complexes described in the introductory chapter of this thesis.

While the 1:2 reaction between [15]crown-5 and $SnBr_2$ did not yield any materials that could be confirmed as the [SnBr([15]crown-5)][$SnBr_3$] salt, the 2:3 reaction of those reagents yielded the sandwich complex [Sn([15]crown-5)$_2$][$SnBr_3$]$_2$, **3.2**[$SnBr_3$]$_2$ (**Scheme 3.2**), which was isolated as analytically pure single crystals after workup. The formation of **3.2**[$SnBr_3$]$_2$ was also confirmed by multinuclear NMR spectroscopy. As with the [18]crown-6 complex, the crown proton signal in the ^{1}H NMR spectrum at 3.78 ppm is deshielded with respect to the free crown signal confirming the complexation in solution.



Scheme 3.2 Synthesis of **3.2**[$SnBr_3$]$_2$

The structure of **3.2**[$SnBr_3$]$_2$ consists of two [15]crown-5 molecules sandwiching the Sn(II) dication (**Figure 3.4**). The two [$SnBr_3$]$^-$ counter anions are clearly separated from Sn^{2+}, and the closest Br_{anion}-Sn^{2+} approach is 5.065(5) Å (see the extended structure provided in Appendix II). The structure of this sandwich complex is isomorphous with the chloride analogue (which was reported in the related monoclinic $P2_1/a$ setting, Sn-O bond lengths ranging from 2.63(2) to 2.79(1) Å).[8] As mentioned, the salt **3.2**[$SnBr_3$]$_2$ crystallizes in the same monoclinic space group $P2_1/c$ (crystallographic data is given in **Table 3.1**) with one formula unit in the asymmetric unit**.** The tin atom in the cation

$[Sn([15]crown\text{-}5)_2]^{2+}$ is bonded to all five oxygens of each crown **(Figure 3.4**). The distances Sn-O in **3.2** range from 2.648(4) to 2.795(4) Å, which are much longer than a typical Sn-O bond length but are in very good agreement with other analogous sandwich complexes of Sn(II).[6,8,9] The geometry of these sandwich structures is best described as two pentagonal pyramids; the apices of the pyramids join at the tin centre and it appears that the tin atom lies on a crystallographic centre of symmetry. Like the chloride analogue, complex **3.2** does not exhibit a stereochemically active lone pair of electrons and this is most likely attributable to the highly symmetrical environment.[8] The structure of **3.2** clearly shows the tin center residing outside the cavity of the two [15]crown-5 moieties (**Figure 3.4**), suggesting that the crown ether is too small to accommodate a Sn^{2+} ion within its cavity. Typically, when the radius of a metal ion (the ionic radii for Sn^{2+} is 0.93Å) is larger than the radius of the ligand cavity (radius of [15]crown-5 is estimated at 0.85 Å), the metal ion is bound in a *facial*-like manner by one ligand to generate an half-sandwich complex (also called *sunrise*), or a sandwich complex when is bound by two ligands.[10]

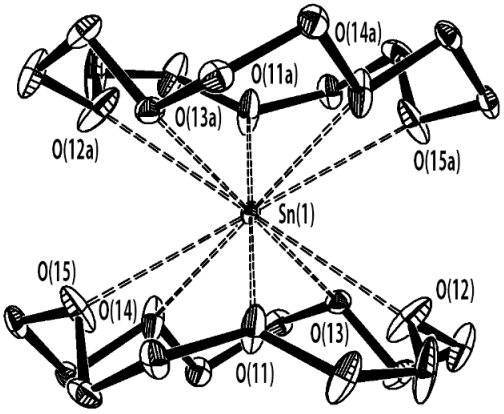
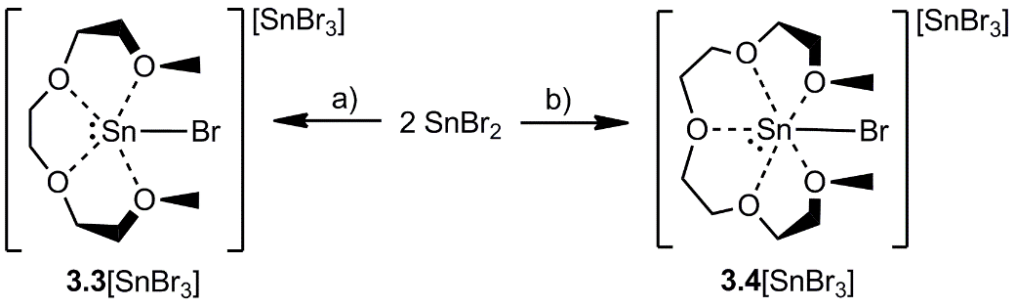


Figure 3.4 Thermal ellipsoid plot (50% probability surface) of **3.2**$[SnBr_3]_2$. Hydrogen atoms and anions are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn1-O11, 2.662(4); Sn1-O12, 2.648(4); Sn1-O13, 2.795(4); Sn1-O14, 2.740(4); Sn1-O15,

2.770(3); O1-Sn1-O2, 60.27(13); O2-Sn1-O3, 59.89(13); O3-Sn1-O4, 59.52(13); O4-Sn1-O5, 60.23(11); O5-Sn1-O1, 61.08(11).

3.2.2 Tin (II) Bromide Glyme Complexes

As with the previously described germanium examples, we sought to also examine the ligand redistribution of $SnBr_2$ using glymes. Though our group had reported tetraglyme and triglyme complexes of tin(II) triflates,[3] there have only been two other structurally authenticated examples of such complexes since then, and recently such complexes have received attention as metal-containing ionic liquid precursors for high-speed metal electrodeposition.[11,12] Synthesis of the glyme complexes [SnBr(triglyme)][$SnBr_3$], **3.3**[$SnBr_3$], and [SnBr(tetraglyme)][$SnBr_3$], **3.4**[$SnBr_3$] was accomplished by treatment of 2 equivalents of $SnBr_2$ with one equivalent of triglyme and tetraglyme, respectively (**Scheme 3.3)**. For both reactions, deshielding of the ^{1}H NMR glyme signals upon coordination is observed, and analytically pure single crystalline materials were obtained upon workup by slow evaporation of THF filtrates.



Scheme 3.3 Synthesis of **3.3**[$SnBr_3$] and **3.4**[$SnBr_3$]; a) triglyme, b) tetraglyme

The salt [SnBr(triglyme)][$SnBr_3$] crystallizes in the monoclinic space group $P2_1/c$ and crystallographic data are given in **Table 3.2.** The crystal structure of **3.3**[$SnBr_3$]

features one crystallographically unique $[SnBr(triglyme)]^+$ fragment where the triglyme complexes the Sn atom in a meridional fashion (**Figure 3.5**). The Sn-Br distance is 2.6751(7) Å and the Sn-O distances range from 2.472(3) to 2.585(3) Å, whereby the terminal O atoms are farther from the Sn atom. Inspection of the packing structure reveals that (unlike the analogous germanium(II) complex) two of these cations form intermolecular contacts between their $[SnBr]^+$ fragments of 3.2552(7) Å, which falls within the sum of the van der Waals radii for Sn (2.19 Å) and Br (1.85 Å).[6,7] While this type of head-to-tail dimerization has been observed for tin(II) chloride fragments (usually featuring strong covalently bound ligands),[13–16] it is much more rare for cases involving tin(II) bromide,[17–20] and the contacts in this instance are very short compared to most other examples.

The Sn1-Br11 distance of 2.6751(7) Å and the average of 2.6658(7) Å of all three Sn-Br distances in the counterion $[SnBr_3]^-$ are comparable to those in complex **3.1**$[SnBr_3]$ and also consistent with literature values.[4,19] The distance of 8.0211(13) Å between Sn_{cation}-Sn_{anion} and distance of 6.3376(13) Å (the shortest of all three Sn_{cation}-Br_{anion} distances) between the anionic bromide and the cationic tin are both significantly longer distances indicating that there is no interaction between the anion and the cation (the extended structure is illustrated in Appendix II). Similar to the structure of **3.1**, the $SnBr^+$ fragment lies nearly normal to the triglyme plane (**Figure 3.5**).

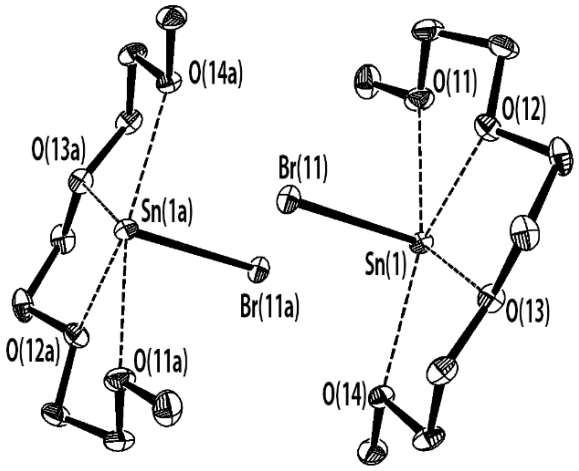


Figure 3.5 Thermal ellipsoid plot (50% probability surface) of **3.3**[$SnBr_3$]. Hydrogen atoms and anions are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn1-Br11, 2.6751(7); Sn1-Br11a, 3.2552(7); Sn1-O11, 2.582(3); Sn1-O12, 2.472(3); Sn1-O13, 2.475(3); Sn1-O14, 2.585(3); Br1-Sn1-O11, 90.04(7); Br1-Sn1-O13, 84.43(7); Br1-Sn1-O14, 84.67(6).

As previously mentioned, the ^{1}H and ^{13}C NMR chemical shifts confirm complexation by triglyme in solution, the signals being considerably deshielded compared to those of the free glyme. The ^{1}H NMR resonances range from 3.50 to 3.86 ppm and the ^{13}C NMR chemical shifts range from 58.43 to 70.48 ppm.

The crystal structure of **3.4**[$SnBr_3$] (**Figure 3.6**) does not feature the same type of intermolecular contacts as the triglyme derivative due to the two additional O-donor atoms, which completely contour the Sn atom. This salt crystallizes in space group $P2_1/c$ (**Table 3.2**) and the same trend of increased Sn-O bond length for the O atoms at the ends of the tetraglyme is observed, with Sn-O bond distances ranging from 2.434(3) Å for the central O atom to 2.715(4) Å for one of the terminal O atoms. The Sn-Br distance of 2.6155(7) Å is slightly shorter than 2.6751(7) Å of the triglyme complex and longer than 2.5979(11) Å of the [18]crown-6 complex. Examination of the structure indicates that the $SnBr^{+}$ fragment

is positioned almost perpendicular to the plane defined by the four oxygen atoms, as seen in similar structures of crown ethers and glymes.

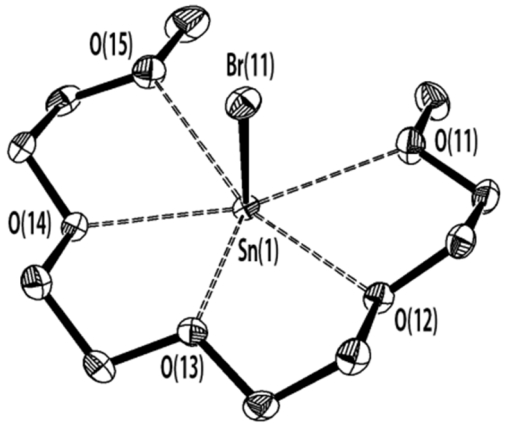


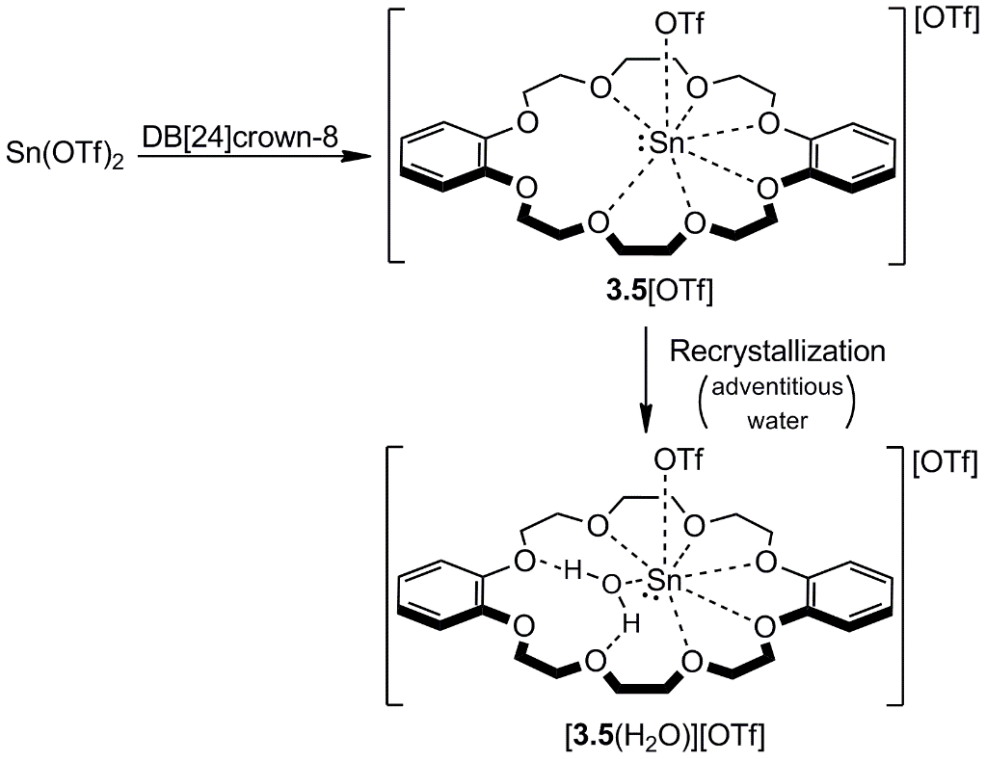
Figure 3.6 Thermal ellipsoid plot (50% probability surface) of **3.4**[$SnBr_3$]. Hydrogen atoms and anions are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn1-Br11, 2.6155(7); Sn1-O11, 2.666(4); Sn1-O12, 2.556(4); Sn1-O13, 2.453(4); Sn1-O14, 2.551(4); Sn1-O15, 2.715(4); Br1-Sn1-O11, 86.39(10); Br1-Sn1-O12, 85.95(8); Br1-Sn1-O13, 82.60(11); Br1-Sn1-O14, 90.41(10).

As in the case of the triglyme complex, the signals in ^{1}H and ^{13}C NMR spectra are deshielded, confirming complexation by tetraglyme in solution. The ^{1}H NMR resonances range from 3.42 to 3.83 ppm and the ^{13}C NMR chemical shifts range from 58.8 to 71.87 ppm.

In all of these complexes (except the sandwich complex of [15]crown-5) the crown ether or the glyme binds the tin atom in a belt-like arrangement, reminiscent of the crown ether complexes with metals from s-block; examples of these complexes have been described in Chapter 1 of this thesis.

3.2.3 Water Complex of Tin(II) Cation

As with germanium, the complexation of tin(II) using larger crown ether ligands has not been explored extensively. Thus, we investigated the synthesis, isolation and the potential reactivity of analogous complexes of tin (II) bromide and tin(II) triflate with dibenzo[24]crown-8. We obtained similar results as with the synthesis of germanium(II) chloride complex with the same crown ether and isolation of the water complex described in Chapter 2. Remarkable results were obtained with the reaction between dibenzo[24]crown-8 and tin(II) triflate. The treatment of equimolar amounts of dibenzo[24]crown-8 with $Sn(OTf)_2$ in DCM resulted in the formation of a white material characterized as [Sn(dibenzo[24]crown-8)OTf][OTf], **3.5**[OTf] (**Scheme 3.4**). Recrystallization of this product from DCM generated crystals of the water complex [(H_2O)Sn(dibenzo[24]crown-8)OTf][OTf], [**3.5**(H_2O)][OTf] presumably due to adventitious amounts of water in the solvent used. The crystals were suitable for examination by single crystal X-ray diffraction. The formation of the water complex [**3.5**(H_2O)][OTf] was further confirmed by elemental analysis, multinuclear NMR spectroscopy and FTIR studies of the isolated crystals.



Scheme 3.4 Synthesis of **3.5** [OTf] and isolation of [**3.5**(H_2O)][OTf]

The complex [**3.5**(H_2O)][OTf] crystallizes in the monoclinic space group $P2_1/c$ (crystallographic data is given in **Table 3.3**), with one crystallographically unique fragment in the asymmetric unit. The distances between the Sn atom and the crown ether oxygens range from 2.4199(16) to 3.4006(17) Å, while the Sn-OH_2 distance is 2.218(4) Å. Two of the Sn-O_{crown} distances are shorter compared with the other three distances, which are significantly longer. As with the water complex of Ge(II), the protons of the H_2O molecule are hydrogen bonded to the O-atoms of the crown ether, OH-O lengths are 1.98(3) Å and 1.84(4) Å, placing the water molecule within the large cavity of dibenzo[24]crown-8 (**Figure 3.7**).

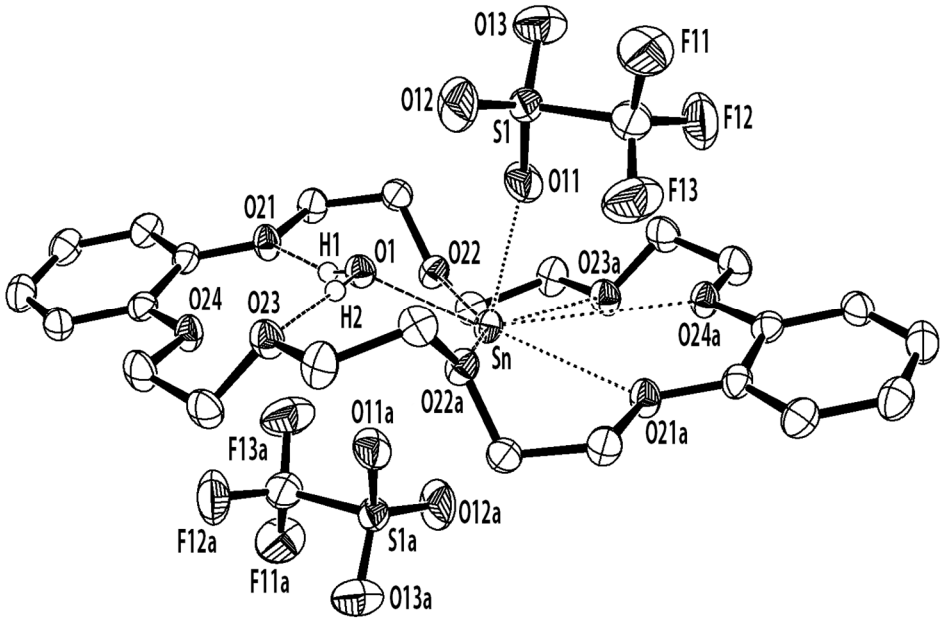


Figure 3.7 Thermal ellipsoid plot (50% probability surface) of [**3.5**(H_2O)][OTf]. Hydrogen atoms (except those on H_2O) are omitted for clarity. Dashed lines are used for Sn-O contacts shorter than 2.5 Å and dotted lines are used to indicate Sn-O contacts longer than 3 Å. Selected interatomic distances (Å): Sn-O1, 2.218(4); Sn-O11, 2.348(19); Sn-O11a, 2.658(2); Sn-O22, 2.4199(16); Sn-O22a, 2.4339(15); Sn-O21a, 3.1680(17); Sn-O23a, 3.0775(17); Sn-O24a, 3.4006(17); S-O11, 1.4505(19); S-O12, 1.424(2); S-O13, 1.421(2); O23-H2, 1.84(4); O21-H1, 1.98(3)

The Sn-$O_{triflate}$ distances in [**3.5**(H_2O)][OTf] are compared with the distances in similar complexes. There is one triflate fragment situated at a distance of 2.3487(9) Å to the tin centre and the other triflate fragment is at 2.658(2) Å. The longer distance lies well within the range of 2.596(9) to 2.741(6) Å for similar Sn(II) complexes.[3] Also, the shorter distance (2.3487(9) Å) is consistent with Sn-$O_{triflate}$ distances found in analogues complexes with two distinct triflate environments.[6] It appears that in similar structures of polyether complexes of tin(II) triflate reported, there is one tin-bound triflate substituent and one "free" triflate anion.[3,4,6] As an example, in the case of the salt [Sn([18]crown-6)OTf][OTf] reported by our group in 2010, the distances between tin and the two triflate ions are

2.282(6) Å for the bound substituent and 2.596(9) Å for the "free" triflate anion.[6] The S-O distances are also considered and compared to the literature values; there are two shorter distances of 1.421(2) Å and 1.424(2) Å and a longer distance of 1.4505(19) Å for S-O11 (**Figure 3.7**) consistent with the reported values for a bound triflate anion.[2,3,6]

Multinuclear NMR spectroscopy and FTIR studies further confirmed the formation of this remarkable water complex. The ^{1}H NMR spectrum of the crystals clearly indicates the presence of the water protons, which appear as a broad peak at 5.61 ppm. The FTIR spectrum of the solid, illustrated in **Figure 3.8**, contains a peak at 3286 cm^{-1} which clearly indicates the presence of H-bonded O-H stretch.

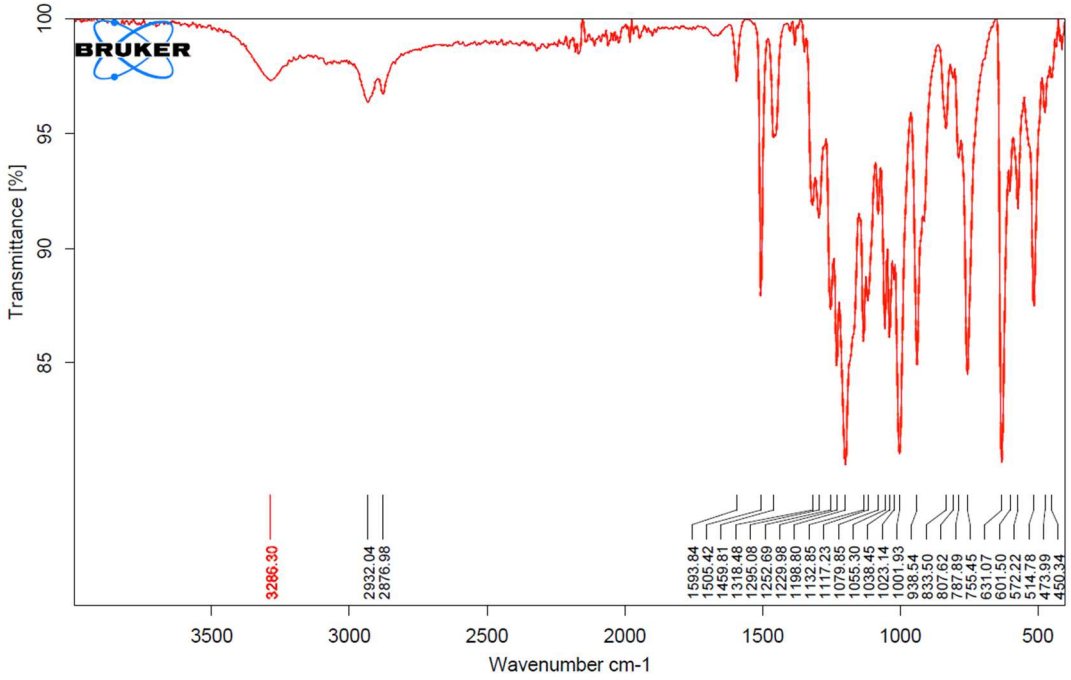


Figure 3.8 FTIR spectrum of [**3.5**(H_2O)][OTf]

3.3 Conclusions

We examined in detail the reactions between tin(II) bromide with three differently sized crown ethers and two glymes ligands. The salts [SnBr([18]crown-6)][$SnBr_3$], [Sn([15]crown-5)$_2$][$SnBr_3$]$_2$, [SnBr(triglyme)][$SnBr_3$] and [SnBr(tetraglyme)][$SnBr_3$] were synthesized and fully characterized including by X-ray crystallography. The new complexes were compared to the chloride and triflate analogues complexes of tin(II) previously reported by our group and other research groups. The reaction between tin(II) triflate and dibenzo[24]crown-8 was investigated as well, and a remarkable water adduct of [Sn(dibenzo[24]crown-8)OTf][OTf] was isolated. The water complex was characterized by X-ray crystallography and confirmed by elemental analysis, multinuclear NMR spectroscopy and FTIR studies. Further chemistry, including synthesis of new complexes of dibenzo[24]crown-8 with $SnBr_2$, deprotonation of the water complex [**3.5**(H_2O)][OTf] and reactivity of tin(II) triflate complex with ammonia, is currently being investigated.

3.4 Experimental

3.4.1 General procedures

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma Aldrich. MeCN-d_3 was dried over calcium hydride or phosphorus pentoxide and stored over molecular sieves under nitrogen. All other solvents were dried on a series of Grubbs' type columns and were degassed prior to use.[21] Glymes were dried over 3Å molecular sieves and degassed prior to use. NMR

spectra were recorded at room temperature on Bruker Avance III 500 MHz, Bruker Avance Ultrashield 300 MHz or Bruker Avance DPX 300 MHz spectrometers. Chemical shifts (δ) are reported in ppm relative to internal standards for ^{1}H and ^{13}C (for the given deuterated solvent). The ^{19}F NMR spectra were referenced externally to $CFCl_3$. Elemental analysis was performed at the University of Windsor Mass Spectrometry Service Laboratory using a Perkin Elmer 2400 combustion CHN analyzer. FT-IR spectra were obtained using a Bruker Alpha FT-IR spectrometer equipped with a Platinum single reflection diamond ATR module; stretching frequencies are reported in cm^{-1}. Melting points were determined under a N_2 atmosphere. Electrospray ionization mass spectrometry was attempted at the McMaster Regional Centre for Mass Spectrometry but none of the species herein withstand the ionization process, and only alkali metal-crown complexes are typically observed in the spectra.

3.4.2 Specific procedures

Synthesis of [SnBr([18]crown-6)][$SnBr_3$], 3.1[SnBr3]

A solution of [18]crown-6 (0.094 g, 0.36 mmol) in THF (ca. 1 mL) was added to a solution of $SnBr_2$ (0.200 g, 0.718 mmol) in THF (ca. 40 mL). The reaction mixture was left to stir overnight at room temperature. After resting without stirring, the clear supernatant was decanted from the white precipitate which was left to dry and characterized as the titled compound. Single crystals suitable for X-ray diffraction studies were obtained through slow evaporation of the clear supernatant. **Yield:** 85% (0.252 g, 0.306 mmol). **Mp:** 167 - 170°C. **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.78 (s). **$^{13}C\{^{1}H\}$ NMR (CD_3CN, 300 MHz) δ:** 70.66 (s). **Anal. Calcd** for $C_{12}H_{24}Br_4Sn_2O_6$: C, 17.55; H, 2.95. Found: C, 18.27; H, 3.08.

Synthesis of [Sn([15]crown-5)$_2$][SnBr$_3$]$_2$, 3.2[SnBr$_3$]$_2$

[15]Crown-5 (0.165 mL, 0.835 mmol) was added to a solution of $SnBr_2$ (0.350 g, 1.26 mmol) in THF (40 mL). The reaction mixture was left to stir overnight at room temperature. After resting without stirring, the clear supernatant was decanted from the white precipitate, which was left to dry and characterized as the titled compound. Single crystals suitable for X-ray diffraction studies were obtained through slow evaporation of the clear supernatant. **Yield:** 90% (0.482 g, 0.377 mmol). **Mp:** 147 – 149 °C. **^{1}H NMR (CD$_3$CN, 300 MHz) δ:** 3.78 (s). **^{13}C{^{1}H} NMR (CD$_3$CN, 300 MHz) δ:** 70.3 (s). **Anal. Calcd** for $C_{20}H_{40}Br_6Sn_3O_{10}$: C, 18.82; H, 3.15. Found: C, 18.13; H, 3.19.

Synthesis of [SnBr(triglyme)][SnBr$_3$], 3.3[SnBr$_3$]

A solution of triglyme (0.132 mL, 0.730 mmol) in THF (ca. 1 mL) was added dropwise to a solution of $SnBr_2$ (0.400 g, 1.44 mmol) in THF (40 mL). The resultant colourless solution was stirred overnight, after which all volatile components were removed under reduced pressure to afford a colourless oil. The oil was washed and sonicated with a 1:1.5 mixture of ether:pentane and dried in vacuo to yield the analytically pure title compound. Crystals suitable for SC-XRD were obtained by slow evaporation of a THF solution. **Yield:** 74% (0.392 g, 0.533 mmol). **Mp:** 86 – 88°C. **^{1}H NMR (CD$_3$CN, 300 MHz) δ:** 3.50 (s, 6H), 3.68 (m, 4H), 3.86 (m, 8H). **^{13}C{^{1}H} NMR (CD$_3$CN, 300 MHz) δ:** 58.43 (s), 69.60 (s), 70.40 (s), 70.48 (s). **Anal. Calcd** for $C_8H_{18}Br_4Sn_2O_4$: C, 13.07; H, 2.47. Found: C, 13.67; H, 2.44.

Synthesis of [SnBr(tetraglyme)][$SnBr_3$], 3.4[$SnBr_3$]

A solution of tetraglyme (0.158 mL, 0.718 mmol) in THF (ca. 1 mL) was added dropwise to a solution of $SnBr_2$ (0.400 g, 1.44 mmol) in THF (40 mL). The resultant colourless solution was stirred overnight, after which all volatile components were removed under reduced pressure to afford a colourless oil. The oil was washed and sonicated with a 1:1.5 mixture of ether: pentane and dried in vacuo to afford the title compound as an analytically pure white powder. Crystals suitable for single x-ray diffraction were obtained by slow evaporation of a THF solution. **Yield:** 92% (0.518 g, 0.664 mmol). **Mp:** 70 – 72 °C. **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.42 (s, 6H), 3.64 (m, 4H), 3.79 (m, 8H), 3.83 (m, 4H). **$^{13}C\{^1H\}$ NMR (CD_3CN, 300 MHz) δ:** 58.8 (s), 70.46 (s), 70.94 (s), 71.12 (s), 71.87(s). **Anal. Calcd** for $C_{10}H_{22}Br_4Sn_2O_5$: C, 15.41; H, 2.85. Found: C, 15.64; H, 2.85.

Synthesis of [SnOTf(dibenzo[24]crown-8)][OTf], 3.5[OTf] and isolation of [3.5(H_2O)][OTf]

A solution of dibenzo[24]crown-8 (0.100 g, 0.223 mmol) in DCM (ca. 1 mL) was added to a solution of $Sn(OTf)_2$ (0.100 g, 0.240 mmol) in DCM. After stirring overnight at room temperature all volatile components were removed under reduced pressure. The resultant white solid was washed with hexanes (4 mL x 2) and allowed to dry, yielding the analytically pure compound. Recrystallization of this material by slow evaporation of DCM yielded a single crystal of **[3.5(H_2O)][OTf]** suitable for SC-XRD, presumably due to adventitious water in the DCM. **Yield:** 89% (0.171 g, 0.198 mmol). **^{1}H NMR (CD_3CN, 300 MHz) δ:** 3.90 (s, 8H), 4.03 (m, 8H), 4.25 (m, 8H), 5.61 (s, 2H, H_2O), 7.06 (m, 8H).**$^{13}C\{^1H\}$ NMR (CD_3CN, 300 MHz) δ:** 69.45 (s), 69.78 (s), 70.45 (s), 115.77 (s), 122.96 (s), 149.5 (s).**$^{19}F\ \{^1H\}$ NMR (CD_3CN, 500 MHz) δ: −79.9 ppm (s). Anal. Calcd**

for $C_{26}H_{32}F_6Sn_2O_{14}S_2$: C, 36.09; H, 3.73. Found: C, 36.28; H, 3.85. **FTIR**: O-H = 3286 cm^{-1}.

3.4.3 X-ray crystallography

Crystals for investigation were covered in Paratone®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N_2 of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXIII software suite[22] on a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with MoK_α (λ = 0.71073 Å) or CuK_α (λ = 1.54178 Å) radiation. For each sample, data were collected at low temperature. APEXIII software was used for data reductions and SADABS[23] was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX[24] software suite as implemented in the WinGX[25] or OLEX2[26] program suites. Validation of the structures was conducted using PLATON[27] and the structures have been deposited in the Cambridge Structural Database (CCDC 1813785-1813794). As with many complexes of this type, several of the compounds exhibited disorder within the polyether groups; this was treated with variable occupancy 2-site models in which appropriate restraints were used to restrain the thermal parameters of related atoms to be approximately equal. Compound **3.1**[$SnBr_3$] was solved as a 2-component twin in P-1; all attempts to solve it in higher symmetry space groups led to unstable refinements or residual factors greater than 0.5.

Table 3.1 Summary of crystallographic data and refinement details for **3.1[$SnBr_3$]** and **3.2[$SnBr_3$]$_2$**

Compound	**3.1[$SnBr_3$]**	**3.2[$SnBr_3$]$_2$**
CCDC	1813791	1813792
Empirical formula	$C_{12}H_{24}Br_4O_6Sn_2$	$C_{20}H_{40}Br_6O_{10}Sn_3$
Formula weight	821.33	1276.05
Color, habit	Colorless, prism	Colorless, prism
Crystal size/mm^3	0.293 × 0.181 × 0.177	0.667 × 0.220 × 0.220
Temperature/K	170(2)	143(2)
Crystal system	Triclinic	Monoclinic
Space group (ASP)	P-1	$P2_1/c$
a/Å	16.1157(18)	10.5528(7)
b/Å	16.116	20.2328(12)
c/Å	20.679(3)	8.8778(5)
α/°	90	90
β/°	90	111.225(3)
γ/°	120	90
Volume/Å^3	4651.1(8)	1766.94(19)
Z	8	2
ρ_{calc}g/cm^3	2.346	2.398
μ/mm^{-1}	9.042	8.932
F(000)	3072	1200.0
Radiation	MoKα	MoKα
Reflections collected	134430	130246
Independent reflections	21429	5153
R_{int}	0.062	0.049
Data/restraints/parameters	21429/0/866	5153/0/178
Goodness-of-fit on F2	1.030	1.128
Final R indexes [I>=2σ (I)]	R_1 = 0.034 wR_2 = 0.070	R_1 = 0.040 wR_2 = 0.0880
Final R indexes [all data]	R_1 = 0.060 wR_2 = 0.081	R_1 = 0.042 wR_2 = 0.089
Residual density / e Å^{-3}	1.142/-1.977	2.99/-1.96
Data completeness / %	99.9	99.9
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F2	
R1(F): {Σ(|F_o| - |Fc|)/Σ|F_o|} for reflections with F_o > 4(Σ(F_o)). wR2(F2): {Σw(|F_o|2 - |Fc|2)2/Σw(|F_o|2)2}1/2 where w is the weight given to each reflection		

Table 3.2 Summary of crystallographic data and refinement details for **3.3[$SnBr_3$]** and **3.4[$SnBr_3$]**

Compound	**3.3[$SnBr_3$]**	**3.4[$SnBr_3$]**
CCDC	1813793	1813794
Empirical formula	$C_{16}H_{36}Br_8O_8Sn_4$	$C_{10}H_{22}Br_4O_5Sn_2$
Formula weight	1470.49	779.29
Color, habit	Colorless, irregular	Colorless, plate
Crystal size/mm^3	0.425 × 0.258 × 0.158	0.388 × 0.306 × 0.055
Temperature/K	143.2	143.21
Crystal system	Monoclinic	Monoclinic
Space group (ASP)	$P2_1/c$	$P2_1/c$
a/Å	9.724(2)	13.9519(11)
b/Å	9.254(2)	11.5896(9)
c/Å	20.207(5)	13.0100(11)
α/°	90	90
β/°	92.466(7)	94.593(3)
γ/°	90	90
Volume/$Å^3$	1816.7(7)	2096.9(3)
Z	2	4
$\rho_{calc}g/cm^3$	2.688	2.468
μ/mm^{-1}	11.549	10.017
F(000)	1352.0	1448.0
Radiation	MoKα	MoKα
Reflections collected	111312	120453
Independent reflections	11803	9946
R_{int}	0.059	0.053
Data/restraints/parameters	11803/0/165	9946/0/192
Goodness-of-fit on F2	1.255	1.305
Final R indexes [I>=2σ (I)]	R_1 = 0.066 wR_2 = 0.104	R_1 = 0.070 wR_2 = 0.124
Final R indexes [all data]	R_1 = 0.083 wR_2 = 0.109	R_1 = 0.079 wR_2 = 0.127
Residual density / e $Å^{-3}$	1.67/-2.17	2.79/-3.74
Data completeness / %	96.2	97.0
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F2	
R1(F): {Σ(|F_o| - |Fc|)/Σ|F_o|} for reflections with F_o > 4(Σ(F_o)). wR2(F2): {Σw(|F_o|2 - |Fc|2)2/Σw(|F_o|2)2}1/2 where w is the weight given to each reflection		

Table 3.3 Summary of crystallographic data and refinement details for **[3.5(H_2O)][OTf]**

Compound	**[3.5(H_2O)][OTf]**
Empirical formula	$C_{26}H_{34}F_6O_{15}S_2Sn$
Formula weight	883.34
Color, habit	Colorless, irregular
Crystal size/mm^3	0.140 × 0.120 × 0.090
Temperature/K	210(2)
Crystal system	Monoclinic
Space group (ASP)	$P2_1/c$
a/Å	10.9349(9)
b/Å	9.1788(9)
c/Å	16.8229(15)
α/°	90
β/°	98.253(3)
γ/°	90
Volume/$Å^3$	1671.0(3)
Z	2
$\rho_{calc}g/cm^3$	1.756
μ/mm^{-1}	0.992
F(000)	892.0
Radiation	MoKα (λ = 0.71073)
Reflections collected	44241
Independent reflections	4863
R_{int}	0.0690
Data/restraints/parameters	4863/3/241
Goodness-of-fit on F2	1.101
Final R indexes [I>=2σ (I)]	R1 = 0.0382, wR2 = 0.0889
Final R indexes [all data]	R1 = 0.0664, wR2 = 0.1084
Residual density / e $Å^{-3}$	0.52/-1.10
Data completeness / %	100
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
R1(F): {Σ(|F_o| - |Fc|)/Σ|F_o|} for reflections with F_o > 4(Σ(F_o)). wR2(F2): {Σw(|F_o|2 - |Fc|2)2/Σw(|F_o|2)2}1/2 where w is the weight given to each reflection	

3.5 References

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Chapter 4: Conclusions and Future Work

4.1 Conclusions

The main focus of this thesis was the synthesis, structural characterization and potential reactivity of new polyether complexes of germanium and tin in low oxidation state +2. Thus, a series of complexes of crown ethers and glymes with germanium(II) and tin(II) bromide have been synthesized and fully characterized.

Using in-house synthesized $GeBr_2$·dioxane to solve the issue of ammonium contamination found in commercially available $GeBr_2$, the salts [GeBr([15]crown-5)][$GeBr_3$], [GeBr([18]crown-6)][$GeBr_3$], [GeBr(triglyme)][$GeBr_3$], [GeBr(tetraglyme)][$GeBr_3$] were isolated and their crystal structures determined. The latter two complexes represent the first examples of crystallographically confirmed glyme complexes of germanium. The complexation of germanium using larger crown ether ligands has been nearly completely unexplored. Thus, reactions of dibenzo[24]crown-8 ether with $GeBr_2$·dioxane and $GeCl_2$·dioxane have been investigated and the salts [GeBr(dibenzo[24]crown-8)][$GeBr_3$] and [GeCl(dibenzo[24]crown-8)][$GeCl_3$] have been synthesized. The water adduct of the latter salt, [(H_2O)GeCl(dibenzo[24]crown-8)][$GeCl_3$] was characterized by X-ray crystallography. The larger crown ether accommodates the $[GeCl]^+$ fragment and a water molecule within its cavity and represents a rare example of a germanium(II) water adduct.

Commercially available $SnBr_2$ was found not to be contaminated with ammonium, and this precursor was used to synthesize the salts [SnBr([18]crown-6)][$SnBr_3$],

$[Sn([15]crown\text{-}5)_2][SnBr_3]_2$, $[SnBr(triglyme)][SnBr_3]$ and $[SnBr(tetraglyme)][SnBr_3]$, each of which was fully characterized including by X-ray crystallography. As with germanium(II), the complexation of tin(II) using larger crown ether ligands has not been explored extensively. Remarkable results were obtained with the reaction between dibenzo[24]crown-8 and tin(II) triflate. The reaction of dibenzo[24]crown-8 with $Sn(OTf)_2$ afforded the formation of the salt [Sn(dibenzo[24]crown-8)OTf][OTf]. Recrystallization of this salt generated crystals of the water complex $[(H_2O)Sn(dibenzo[24]crown\text{-}8)OTf][OTf]$ suitable for examination by single crystal X-ray diffraction.

It is worth mentioning that these new Ge(II) and Sn(II) polyether complexes exhibit structures in which the germanium or tin atom is "belted" by the crown ether or glyme ligands in a manner reminiscent of s-block metal crown ether complexes. Representative examples of the latter complexes have been described in the first chapter of this thesis.

All these new polyether complexes were structurally characterized and confirmed by elemental analysis and multinuclear NMR spectroscopy. The two germanium and tin water complexes isolated and crystallographically characterized were further confirmed by FTIR studies, the spectra clearly showing the O-H stretches. This hitherto unreported series of compounds compliments the known chloride and triflate analogues, which have only recently been reported.[1,2] We are presently investigating the synthesis of new polyether complexes of germanium(II) triflates with [18]crown-6 and dibenzo[24]crown-8 and tin(II)bromide with dibenzo[24]crown-8 as well as further chemistry involving these species. The potential reactivity of some of the new polyether complexes with simple reagents (i.e. water, ammonia and weak bases) has been explored and the preliminary results are provided and discussed in next section of this chapter.

4.2 Future work: Investigation into the Reactivity of the New Polyether Complexes

In 2013, our research group reported the first stable water and ammonia adducts of germanium(II).[3] In that work, the treatment of [Ge[15]crown-5][OTf]$_2$ with H_2O and NH_3 yielded the remarkable and unexpected complexes given the considerable reactivity of most divalent germanium compounds. Also, it was suggested that deprotonation reactions of the water complex should be possible because of the presence of potentially acidic hydrogen atoms. The reactions of the water adduct with weak bases and relatively strong bases, resulted in the formation of the anticipated conjugate acids.[3]

4.2.1 Reactivity with ammonia

The 1:1 reaction between previously prepared Ge(II) triflate and dibenzo[24]crown-8 in acetonitrile, yielded an oily product, which after washing with hexane provided a white solid confirmed to be the complex with a stoichiometry of Ge(OTf)$_2$·(dibenzo[24]crown-8). Although single crystals suitable for X-Ray diffraction could not be obtained, the proposed complex was confirmed by ^{1}H, ^{13}C and ^{19}F NMR (signal at -80.31 ppm) and by elemental analysis (Anal. Calcd for $C_{26}H_{32}F_6\,GeO_{14}S_2$: C, 38.12; H, 3.94. Found: C, 38.53; H, 4.43). To explore the potential reactivity of this complex with ammonia, a new reaction has been investigated. Thus, the treatment of Ge(OTf)$_2$·(dibenzo[24]crown-8) with a solution of NH_3 in dioxane resulted in the formation of a colorless compound which is expected to be the ammonia complex of Ge(OTf)$_2$·(dibenzo[24]crown-8).

The ^{1}H NMR data and the FTIR studies provided evidence of the complex formation. The ^{1}H NMR spectrum clearly indicates the presence of the coordinated amine protons, which appear as a broad peak at 7.72 ppm. The spectrum also features a 1:1:1 triplet centered at 6.43 ppm, the multiplicity of which is due to coupling of the protons to the ^{14}N isotope (I = 1, 99.63% abundant). The triplet resonance suggests the presence of $[NH_4]^+$ cations in solution, which indicates that due to the complexation of NH_3 the protons have become sufficiently acidic to protonate other ammonia molecules. The FTIR spectrum of the solid contains a broad peak at 3240 cm^{-1} which corresponds to the N-H stretch (**Figure 4.1**).

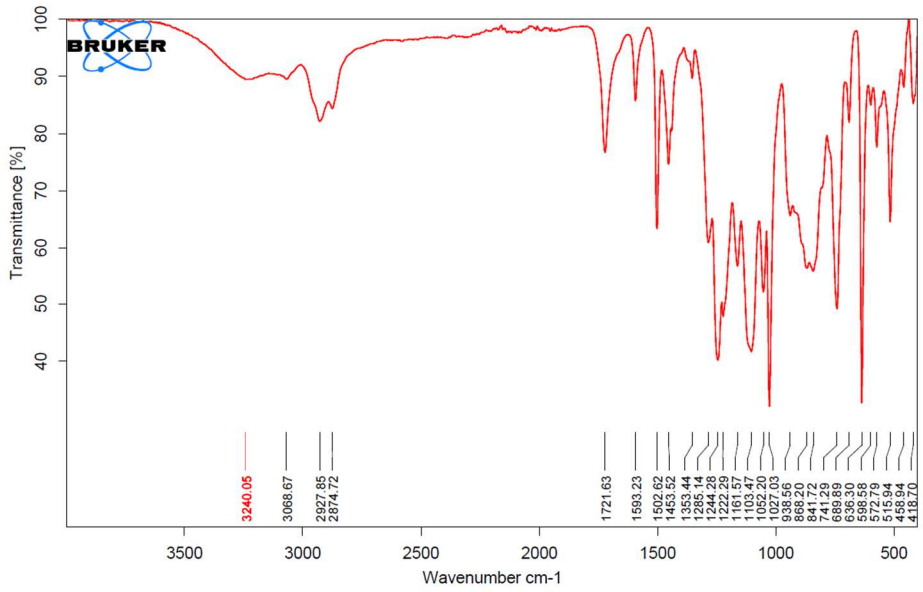

Figure 4.1 FTIR spectrum of ammonia complex of $Ge(OTf)_2$·(dibenzo[24]crown-8).

Although we have not yet been able to obtain single crystals for these complexes, the first results obtained are promising and provide important evidence for future work. Further investigation and characterization is required. It is worth emphasizing that these

results are comparable to those reported for the ammonia complex of [Ge[15]crown-5][OTf]$_2$.[3]

4.2.2 Deprotonation of the Water Complex

It has been observed that the acidity of the water and ammonia increased upon complexation. The presence of potentially acidic hydrogen atoms on the water fragment in [Ge[15]crown-5(H_2O)][OTf]$_2$ has been confirmed through reactions with weak bases and relatively strong bases.[3]

Deprotonation of the new water adduct [(H_2O)GeCl(dibenzo[24]crown-8)][$GeCl_3$] by using weak bases, was investigated and the preliminary results are presented in this section. Two reactions of the water complex with one and two equivalents of N-methylimidazole have been studied. The weak base was added to a colourless solution of [(H_2O)GeCl(dibenzo[24]crown-8)][$GeCl_3$] in DCM. The white precipitate formed was collected by filtration. After the removal of all volatiles from the filtrate, the white residue was washed with toluene. The second white precipitated was characterized by ^{1}H NMR and expected to be the conjugate acid. The colourless oil resulted after the removal of all volatiles from the filtrate was also assessed by ^{1}H NMR and expected to contain the crown ether fragment. Although further investigation is required, the examination of the preliminary data provides evidence of these deprotonation reactions. The first results of the reaction with one equivalent of N-methylimidazole are comparable to those of the first water adduct of [15]crown-5 complex[3] and indicate a mono-deprotonation reaction (^{1}H NMR spectrum of the first reaction is illustrated in **Figure 4.2**). This preliminary data requires further confirmation but the first results are promising. For this reaction, further

work to subsequently separate the products is required. ^{1}H NMR spectra for the reactions with two equivalents of N-methylimidazole are provided in the supplementary information section (Appendix III). In this case, further NMR studies to confirm the separation of the products will be needed. Suggested future work includes deprotonation of the new water adduct $[(H_2O)GeCl(dibenzo[24]crown-8)][GeCl_3]$ by using relatively strong bases (i.e. proton sponge, N-heterocyclic carbenes).

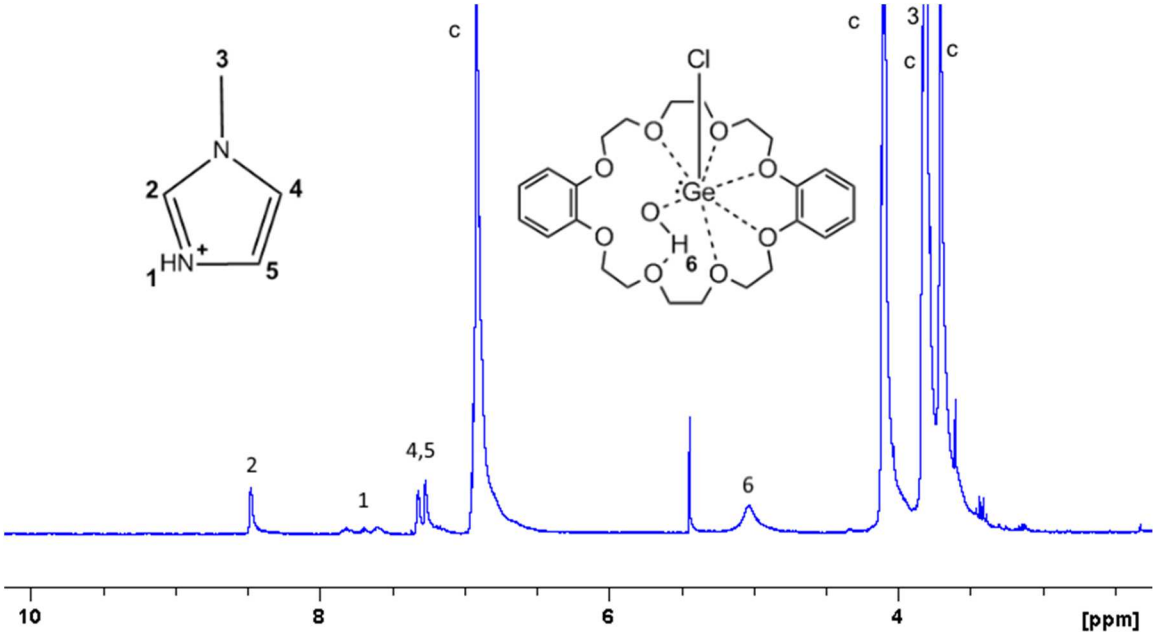

Figure 4.2 ^{1}H NMR spectrum of the reaction of $[(H_2O)GeCl(dibenzo[24]crown-8)][GeCl_3]$ with one equivalent of N-methylimidazole in CD_3CN (C =crown ether; THF at 3.6 ppm and DCM at 5.44 ppm are also present)

4.2.3 Reactivity with water

Given the isolation of the new water complex $[(H_2O)GeCl(dibenzo[24]crown-8)][GeCl_3]$ and the potential reactivity of smaller size

(<[24]crown-8) crown ether complexes of Ge(II) with simple reagents, the reaction with water of Ge(II) bromide and [18]crown-6 complex, previously synthesized and characterized (Chapter 2), was considered for investigation. The addition of one molar equivalent of water to a solution of [GeBr([18]crown-6)][$GeBr_3$] in THF yielded a colourless solution. Removal of all volatile components generated a white solid, which was assessed by ^{1}H NMR spectroscopy in solution. The ^{1}H NMR spectrum (spectrum illustrated in Appendix III) clearly indicates the presence of the water protons, which appear as a broad peak at 6.29 ppm. This value indicates that the protons of the water molecule have become considerably deshielded upon complexation (the resonance for free water in CD_3CN is 2.13 ppm). This change in chemical shift suggests that the protons of the water have become considerably acidic. The increased acidity of the water upon complexation has already been proved by the deprotonation reactions of the water complexes with various bases. The ^{1}H NMR spectrum also shows a signal at 3.78 ppm attributable to the crown ether and this value is consistent with the resonance for the crown in the starting material [GeBr([18]crown-6)][$GeBr_3$]. It is worth remembering that the ^{1}H NMR signals for the crown ether protons in each of the new complexes were significantly deshielded from those of the free crowns.

Unfortunately, single crystals of this material suitable for X-ray diffraction have not yet been obtained. Further work to optimize the recrystallization process of this product and further characterization is required. It should be noted that the addition of a small excess of water does not appear to degrade the compound but the addition of increased amounts of water decomposed the product. These preliminary results indicate the

complexation of the water and confirm the formation of the proposed water adduct $[(H_2O)GeBr([18]crown-8)][GeBr_3]$.

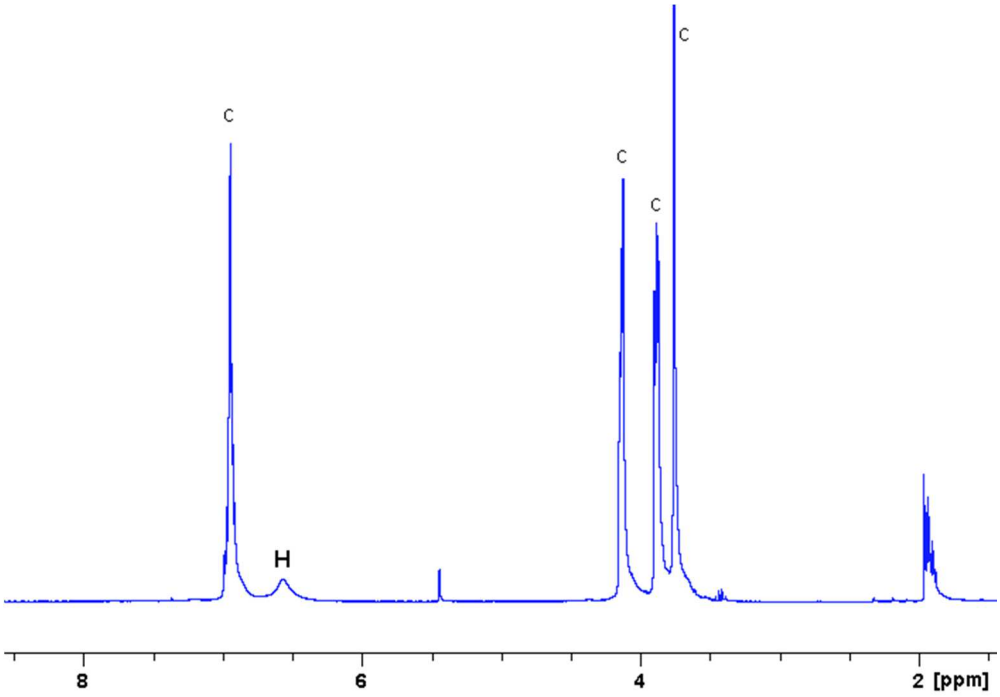

Figure 4.3 ^1H NMR spectrum of the water adduct $[(H_2O)GeCl(dibenzo[24]crown-8)][GeCl_3]$ in CD_3CN (**H= H_2 O**; C =crown ether); THF: 1.8 ppm, Et_2O: 3.42 ppm and DCM: 5.44 ppm are also present.

The reaction between the previously prepared complex $[GeCl(dibenzo[24]crown-8)][GeCl_3$ and water, is worth mentioning. The white powder resulted by the treatment of a solution of $[GeCl(dibenzo[24]crown-8)][GeCl_3]$ in THF with one molar equivalent of water was assessed by ^1H NMR spectroscopy in solution. As previously seen, the ^1H NMR spectrum, illustrated in **Figure 4.3** above, shows the broad peak at 6.57 ppm, which indicates the presence of the water protons and clearly confirms the complexion. FTIR studies further confirmed the formation of the water complex. The FTIR spectrum, provided in Appendix III, contains a peak at 3240 cm^{-1}, which clearly

indicates the presence of H-bonded O-H stretch. In this case, further characterization is not necessary, as this complex has been previously confirmed and fully characterized as the water adduct of [GeCl(dibenzo[24]crown-8)][$GeCl_3$].

Suggested future work includes the synthesis and isolation of the analogue water complex of [GeBr(dibenzo[24]crown-8)][$GeBr_3$] following a similar procedure, and the synthesis of the heavier iodide analogues as well as further chemistry involving these species. Investigations involving the role of these complexes as material precursors and their new synthetic potential (i.e. through O─H activation) are suggested for future studies, too.

Regarding the tin(II) chemistry, a series of tin(II) bromide polyether complexes have been synthesized and fully characterized. We have been synthesised the tin(II) triflate complex with dibenzo[24]crown-8) and isolated the water adduct [(H_2O)Sn(dibenzo[24]crown-8)OTf][OTf]; the results have been discussed previously in chapter 2. Future work will focus on the reactivity of tin(II) complexes with water and ammonia, the deprotonation of these complexes by using different reagents and the synthetic potential of these complexes.

4.3 References

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Appendices

Appendix I: Supplementary Information for Chapter 2

X-ray crystallography

Crystals for investigation were covered in Paratone®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N_2 of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXII software suite[1] on a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with MoK_α ($\lambda = 0.71073$ Å) or CuK_α ($\lambda = 1.54178$ Å) radiation. For each sample, data were collected at low temperature. APEXII software was used for data reductions and SADABS[2] was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX[3] software suite as implemented in the WinGX[4] or OLEX2[5] program suites. Validation of the structures was conducted using PLATON.[6]

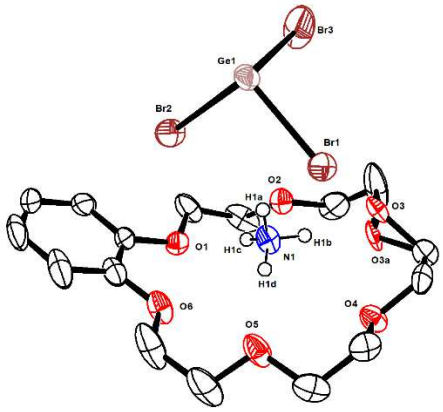

Figure A.1 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of **[NH4(benzo[18]crown-6)][GeBr$_3$]**. Hydrogen atoms (except those on nitrogen) are omitted for clarity.

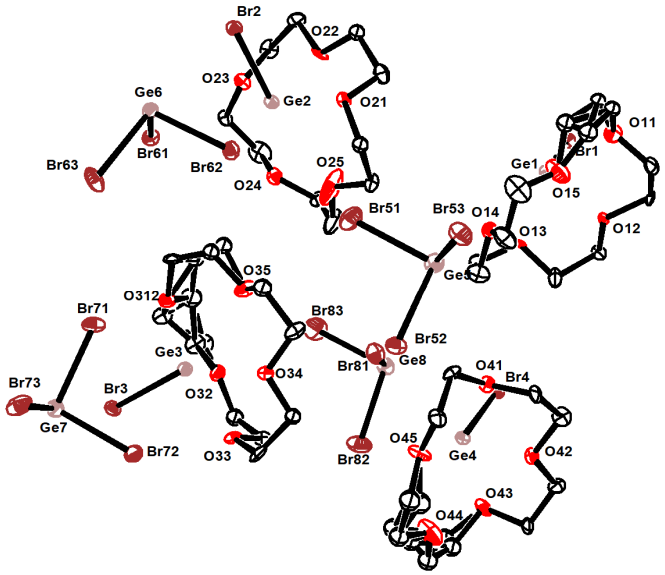

Figure A.2 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of **2.1**[GeBr$_3$]. Hydrogen atoms are omitted for clarity.

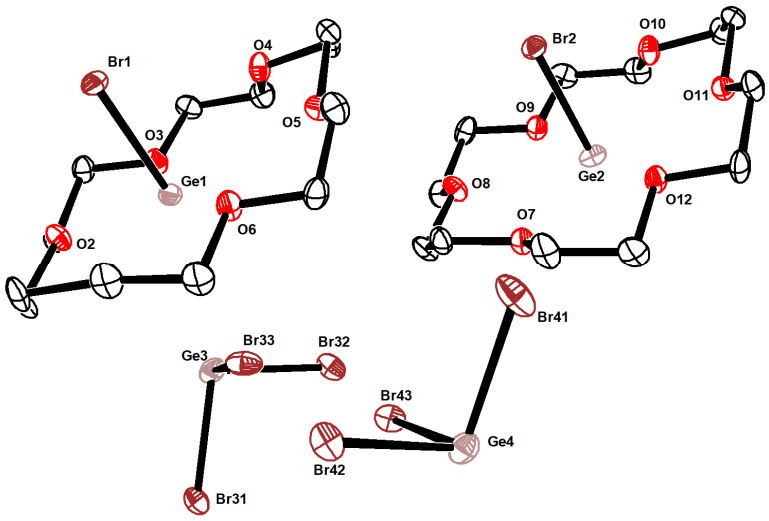

Figure A.3 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of **2.2**[GeBr3]. Hydrogen atoms are omitted for clarity.

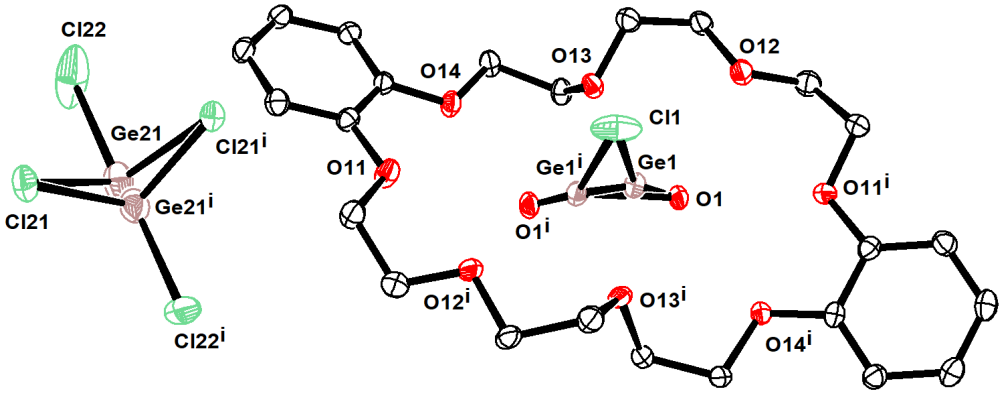

Figure A.4 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of [**2.4**(H2O)][$GeCl_3$]. Hydrogen atoms are omitted for clarity.

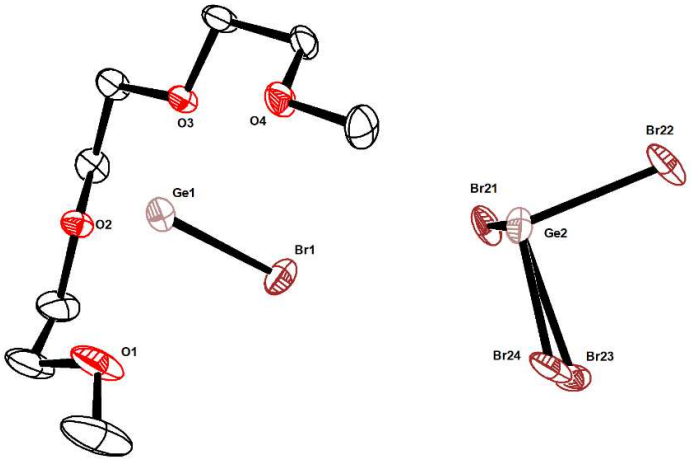

Figure A.5 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of **2.5**[$GeBr_3$]. Hydrogen atoms are omitted for clarity.

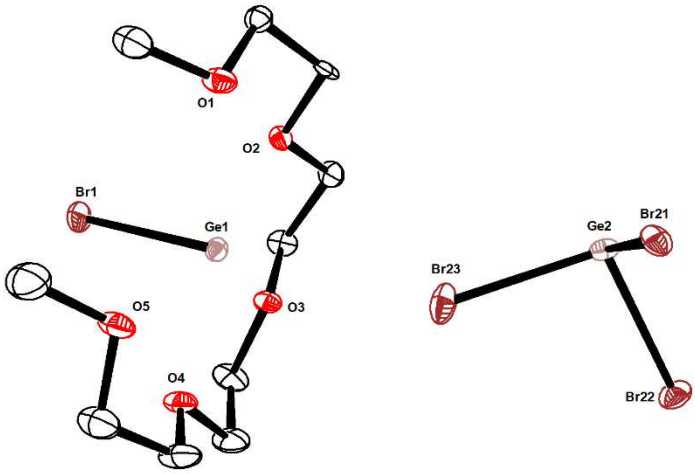

Figure A.6 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of **2.6**[$GeBr_3$]. Hydrogen atoms are omitted for clarity.

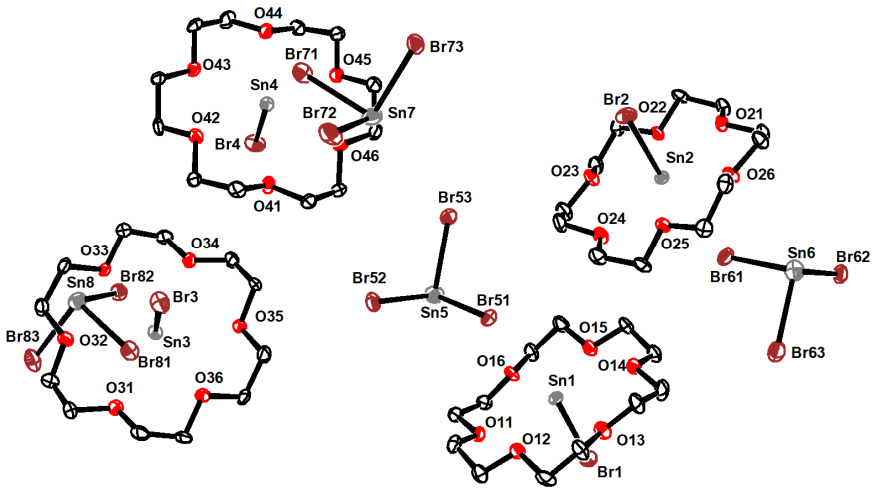

Figure A.7 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of **3.1**[$SnBr_3$]. Hydrogen atoms are omitted for clarity.

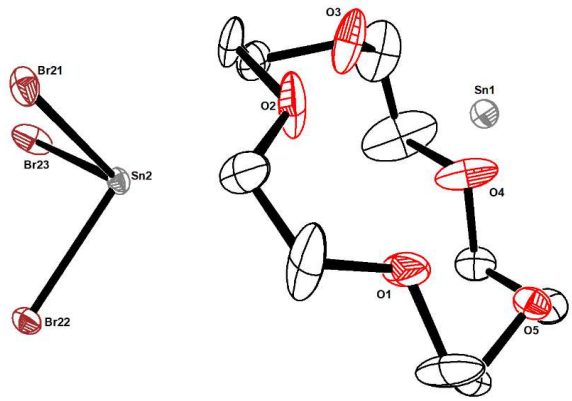

Figure A.8 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of **3.2**[$SnBr_3$]$_2$. Hydrogen atoms are omitted for clarity.

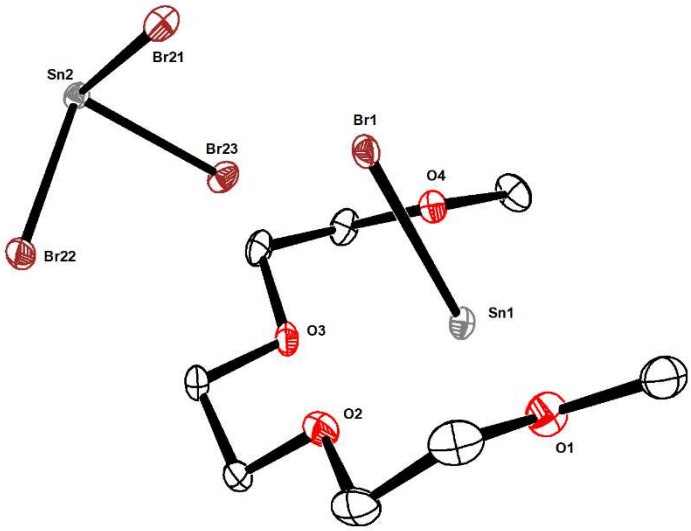

Figure A.9 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of **3.3**[$SnBr_3$]. Hydrogen atoms are omitted for clarity.

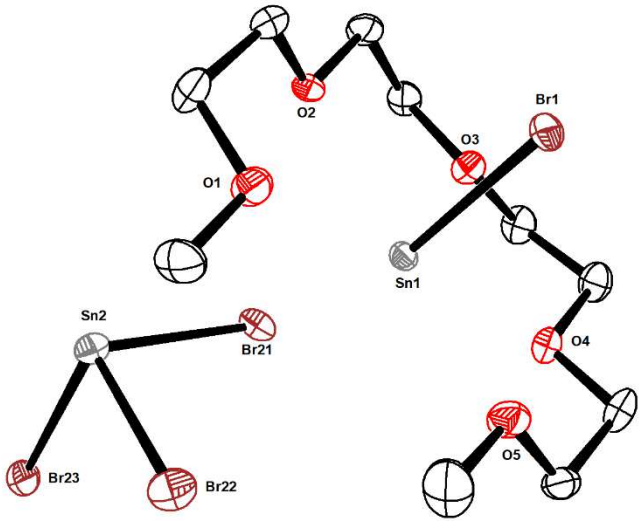

Figure A.10 Thermal ellipsoid plot (50% probability surface) of the asymmetric unit of **3.4**[$SnBr_3$]. Hydrogen atoms are omitted for clarity.

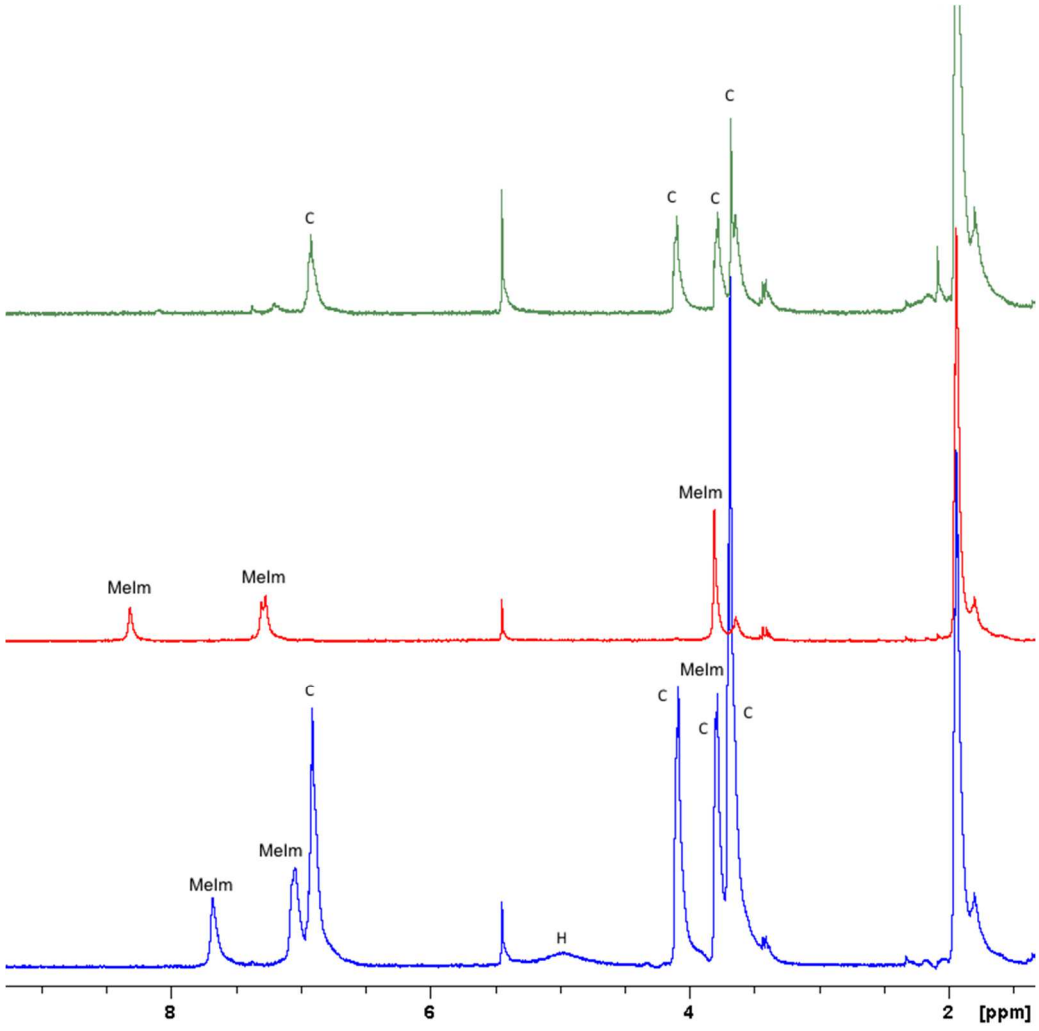

Figure A.11 ^{1}H NMR spectrum of the reaction of $[(H_2O)GeCl(dibenzo[24]crown\text{-}8)][GeCl_3]$ with two equivalent of N-methylimidazole (MeIm) in CD_3CN (H= water; C =crown ether; DCM at 5.44 ppm is also present)

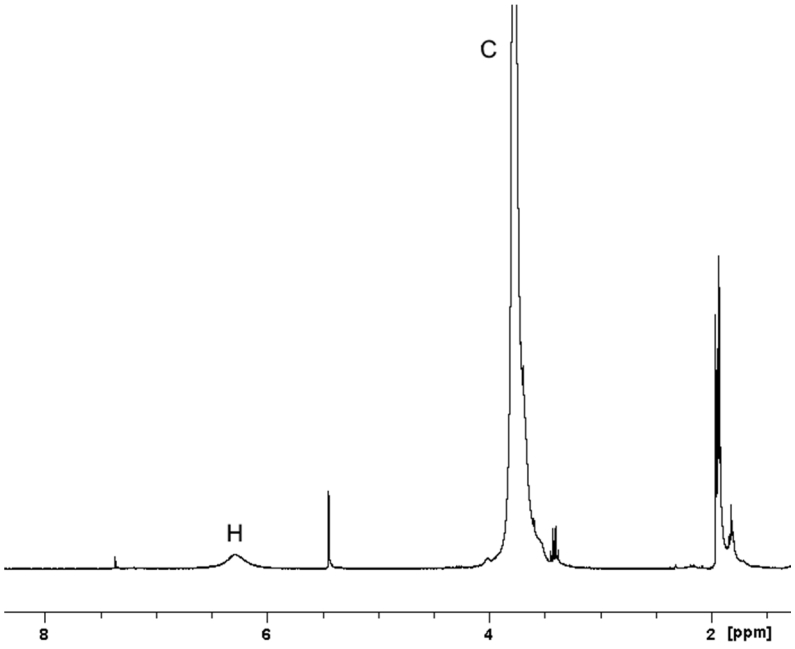

Figure A.12 ^{1}H NMR spectrum of the proposed water adduct of **[GeBr([18]crown-6)][GeBr$_3$]** in CD_3CN (**H= H_2O**; C =crown ether); THF: 1.8 ppm, Et_2O: 3.42 ppm and DCM: 5.44 ppm are also present.

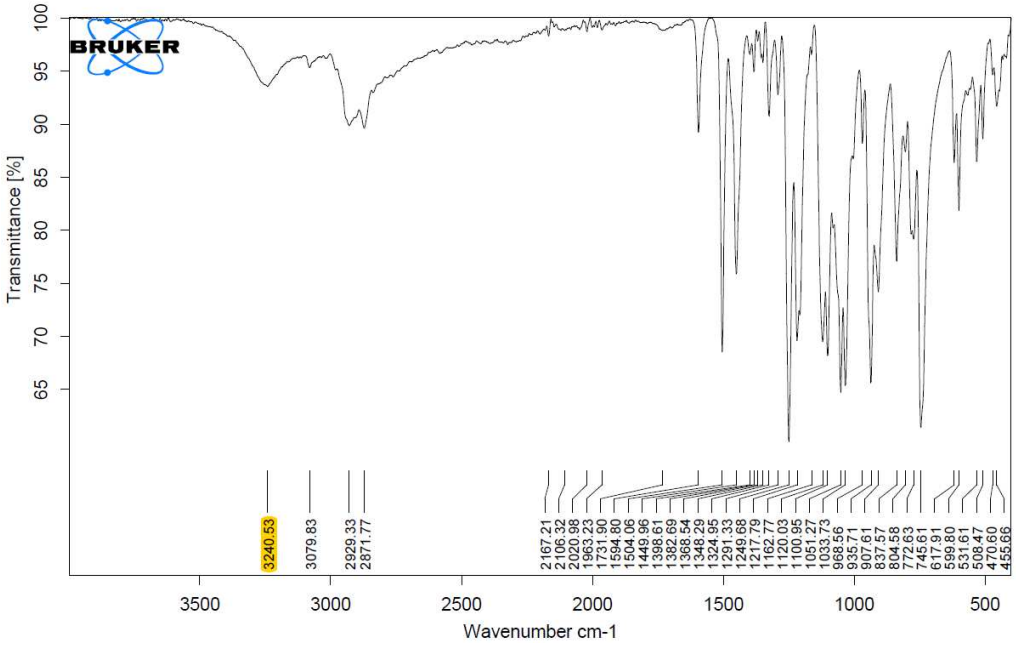

Figure A.13 FTIR spectrum of the water adduct of **[GeCl(dibenzo[24]crown-8)][GeCl$_3$]**.

References

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